Natural Hydraulic Lime Mortars for Use in High Temperature, High Humidity Climatic Conditions: Effect of Calcitic Fillers

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Submitted for the degree of Doctor of Philosophy

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June 2014

ABSTRACT

The widespread adoption of alternative binders are playing an increasing role in carbon dioxide (CO_2) abatement in green construction and the repair of traditionally built structures. Natural Hydraulic Lime (NHL) has better environmental credentials than Portland Cement (PC) due in part to its lower calcination temperature and its ability to absorb CO_2 during carbonation. However, NHL is more sensitive to climatic conditions during the setting and hardening processes and this is especially pronounced in high humidity climates. This research investigated the influence of various types of calcitic fillers (oyster shells, limestone, marble and precipitated calcium carbonate (PCC)) modifications to NHL mortars subjected to high temperature and humidity environments and evaluated the subsequent effect on early development of various chemical and physical properties. Primary mortar parameters such as moisture loss, pH, carbonation depth, flexural strength, compressive strength, sorptivity and microscopy analysis (SEM images) were studied.

The results showed that the setting and hardening of those mortars with precipitated calcium carbonate worked most effectively in high humidity environments. The purity and crystallinity of the mineral ‘seeding’ materials was attributed to the positive benefits in the physical characteristics. Additionally, curing at higher temperatures greatly accelerated the hydration reaction of the mortar. It is evident from the findings that modified mortars can increase the performance especially in terms of carbonation rate, flexural strength, compressive strength and sorptivity. Whilst the precipitated calcium carbonate showed positive benefits in early stage setting reactions it did not significantly influence the long term physical characteristics of the mortars. This situation is meaningful for our understanding of modified lime mortars and the seeding materials. This research can be used to influence the specification and product design of NHL materials in high temperature and high humidity environments and this is especially important for its early stage use that has been traditionally associated with reduced set characteristics.

DEDICATION

To my dearest husband, Khairul Faizal Pa’ee

ACKNOWLEDGEMENTS

In the name of God, the Most Gracious and the Most Merciful

First and foremost, I would like to express my sincere gratitude to my supervisor Dr. Alan M. Forster for the continuous support of my Ph.D study. His sage advice and mentorship helped me in writing of this thesis. I would also like to thank Professor Phil Banfill whose steadfast support of this study was greatly needed and deeply appreciated.

My sincere thanks also go to Ewan Szadurski and Dr. Clare Torney of Historic Scotland for their endless support, guidance and encouragements. Not forgetting Graham Sorley, Alastair MacFarlane, Alex Heron and Dr. Jim Buckman for technical and analytical assistance during this PhD work.

To my dearest friends, Alaa, Menan, Richard B, Francesca, Prince, Kivanc and Nicole; thank you for your friendship, love and support. I wish you all great success and health in the future.

DECLARATION STATEMENT

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NOTATION

C_2S	Dicalcium silicate - Ca_2SiO_4 - Belite
C_3S	Tricalcium silicate - Ca_3SiO_5 - Alite
Ca	Calcium
$Ca(OH)_2$	Calcium hydroxide - portlandite
$CaCO_3$	Calcium carbonate - calcite / vaterite / aragonite
CaO	Calcium oxide - Quick lime
CO_2	Carbon dioxide
C-S-H	Calcium silicate hydrate - H_2CaO_4Si
H_2O	Water
NHL	Natural Hydraulic Lime
O_2	Oxygen
OPC	Ordinary Portland Cement
PCC	Precipitated Calcium Carbonate
SEM	Scanning Electron Microscope
XRD	X-Ray Diffractometer

LIST OF PUBLICATIONS

Forster, A. M., Razali, N., Banfill, P. F. G., Szadurski, E. and Torney, C. (2013) 'The influence of calcitic filler in hydraulic lime mortars for use in high temperature & high humidity climatic conditions: A preliminary investigation', in Hughes, J. J., ed. *3rd Historic Mortar Conference,* Glasgow, Scotland, University of the Western of Scotland.

CHAPTER 1
INTRODUCTION

1.1 Introduction to Lime Mortar

Lime is chemical compound used in the main as a binder for the production of mortars, plasters and renders (Hughes and Valek 2003). Limes can be broadly characterized into two different types; hydraulic and non-hydraulic. Non-hydraulic lime (quicklime or lime putty) consists predominantly of calcium oxide and calcium hydroxide (respectively) and is derived from the calcination of pure limestone. These materials set purely through carbonation. Hydraulic lime is produced from burning limestone containing 'impurities' i.e. clay minerals that are primarily associated with silica. These materials have a dual set reaction in the form of carbonation and hydration. Hydration is synonymous with the ability to set underwater (Oates 1998, Diekamp et al. 2012, Forster 2004b, Forster 2004c).

Lime mortars have been used globally for millennia and regional techniques and manufacture processes have developed to enable their satisfactory use. Its setting properties, durability and workability in the main are favourable and ensured historic uptake of the material (Mallinson and Davies 1987). Lime mortars have been used historically throughout the world, including ancient Egyptian, the Roman Empire and throughout Europe and Africa. Physical and documentary evidence of the use of these materials dates back 2000 years (Hughes and Valek 2003).

Lime has been used for many construction purposes including foundations, walls, floors, vaults and roof and also used as building finishes for example paints, plasters (both decorative and flat work), renders and hand modelled stuccos for aesthetical aspects of building. Lime mortars have been proven to be compatible with historic building materials. Their compatibility with substrate materials enables them to be relatively durable under severe mechanical and environmental loads (Holmes and Wingate 2002).

The recent resurgence in the use of lime mortar within the building industry has increased the demand for knowledge and understanding of its properties. Due to the environmental advantages compared with cement, hydraulic lime based mortars are becoming increasingly specified.

1.2 Benefits of Lime Mortar

Modern literature illustrates the benefits of natural lime over the modern cements that dominate the building industry today. Hydraulic lime is more environmental friendly than Ordinary Portland Cement (OPC) due to lime’s lower firing temperature during the calcination process (Smith et al. 2005). The manufacture of limes (hydraulic and non-hydraulic) consume less energy and produce less greenhouse gases than Ordinary Portland Cement per unit weight (Mahasenan et al. 2003). Furthermore, it reabsorbs carbon dioxide during setting process thus lowering its carbon footprint even further. In addition to optimising the energy efficiency of Portland cement production plants, the amount of cement used in concrete mixes can be reduced by using cement substitutes. Lime binders are one of these substitution materials.

In terms of design, lime mortar is more permeable than cement thus allowing a building to ‘breathe’ by not trapping moisture in a structure’s fabric (Forster 2002, Banfill and Forster 1999). Lime mortar has been shown to reduce rapidity of stone decay. It could save weaker natural substrate material from the harmful effects of thermal and moisture movement. Freezing and thawing cycles associated with moisture are noticeably reduced in walls built with lime mortar, which have been shown to have an increased tolerance to degradation (Hughes and Valek 2003).

1.2.1 Challenges of Using Lime Mortars

The widespread adoption of alternative binders is playing an ever increasing role in carbon dioxide (CO_2) abatement and green construction (Forster et al. 2011). Lime is however perceived as being more sensitive to climatic exposure variations during construction as opposed to OPC. Premature drying is well understood to lead to an adversely altered microstructure development and associated lower strength (Kanna et al. 1998, Un and Baradan 2011). Conversely, a hydraulic lime mortar placed in a high humidity environment will fail to readily carbonate and therefore not attain its full set characteristics. The influence of specific environmental conditions upon the performance of these materials is insufficiently understood (Forster and Carter, 2011).

1.3 Extreme Climatic Conditions and Performance of Lime Mortar

Understanding climate factors is an essential ‘first order’ consideration in designing and building effective and efficient structures (Emmitt and Gorse 2006). Upon completion, structures gradually deteriorate according to the exposure conditions they are subject to, their design and use factors (Tanabe 2008, Forster and Carter 2011). The influence of climate has a major effect on the functionality, life span, environmental performance and durability of construction materials (Uyeda 2009) and the structure as a whole. Oliver (2005) suggested that material stress resulting from adverse climatic conditions is less considered in the working standards of the construction industry. Climatic conditions cause stress to buildings through temperature variations (heat and cold), intensity of solar radiation, atmospheric gases, humidity, rainfall and wind (Dimoudi 2001). Furthermore, environmental conditions will vary according to direction and position of the structure such as north and south elevations which may affect its exposure to phenomenon such as driven rain (Tanabe 2008).

The environmental conditions that a lime mortar is exposed to plays a major role in the evolution of products of hydration and the formation of other mineral compounds, such as calcite (Dotter 2010). The efficacy of formation plays a significant role in determining strength and longer term durability and thereby resistance to deterioration characteristics.

Extreme climates such as those associated with arid conditions can limit the carbonation and curing process. Schroder and Ogletree (2009) indicate that high temperatures during curing may cause high stress in the freshly applied mortars, that interrupt the carbonation process. More importantly, rapid dehydration of the mortar in these conditions is well understood to lead to partial hydration. This results in a low strength, poorly performing material. In addition, arid regions are associated with great variations between day and night temperatures. Compounding this, arid regions receive very little annual rainfall with the climate being governed by the macro climate and is typified as hot and dry (Walker 2002). The absence of cloud in the region also has an influence on prolonged and intense solar radiation that has adverse effects.

The climate in Southeast Asia is mainly tropical and is characterised by hot (with relative temperature stability of approximately 30°C throughout the year) and humid conditions all year round with high levels of rainfall. Additionally, extreme weather events such as typhoons and flooding are particularly prevalent in lower elevation topographical landmasses (Haggett 2002). Southeast Asia has a wet and dry region with season shifts caused by seasonal changes in winds or monsoon (Petersen et al. 2011).

Due to a lack of availability and perceived difficulties with the use of lime materials (including high humidities), the majority of binders used in Malaysian construction are Portland Cement (PC) based. These materials have advantages in terms of solely requiring a hydraulic set reaction for their set propagation and are therefore not adversely affected by high humidity as with low hydraulicity limes (Prezant et al. 2008). Additional wide scale utilisations of PC based mortars are associated with the perceived benefits of impermeability or ‘water-proofing’ characteristics of the relatively dense materials. This attitude is widely discredited especially within the context of historic buildings (Banfill and Forster 1999, Hughes 1986). Lime mortars used in these countries are important to allow the building to ‘breathe’ by not trapping moisture in the wall (Lawrence et al. 2006). Many buildings and houses are built adopting Portland cement bound concrete materials as they are perceived to be durable when subject to heavy rainfall. In a humid tropical climate, defects in rendering and mortars are normally caused by biological growth arising out of penetrating rain, evaporation, condensation, air pollution, dehydration and thermal stress (Ahmad 2004).

1.4 Significance of the Research Programme

Evidence suggests that seeding of lime mortars encourages the early stage precipitation of calcite by accelerated carbonation reaction (Forsyth 2007). Lawrence (2006) concurs indicating that the seeding of lime mortars with 6% finely ground calcite has been shown to improve the rate of carbonation. The addition of calcitic aggregates into lime mortars has many historic precedents and these components are often found in many historic mortars (Hughes and Valek 2003, Gibbons and Newsom 2003). The understanding of the perceived beneficial nature of these aggregates is little understood, however, their serendipitous addition could have inadvertently enhanced performance. In contemporary work, calcitic aggregate additives are used by specifiers and contractors to enhance the initial set in limes in high humidity environments. This is especially common on the West Coast of the United Kingdom, well known for high rainfall and low potential evaporation (Hall and Hoff 2012).

Various researchers suggest there is a possibility to substitute Ordinary Portland Cement with lime binder in certain construction processes (Sickels-Taves and Sheehan 2002, Wilkinson 2009). Lime is clearly not appropriate for all construction processes but is a welcomed addition to the 'palette' of materials for building. Variations in environmental conditions, such as relative humidity and temperature, influence the performance of lime and cement mortars alike. Rapid dehydration of water in a freshly placed hydraulic mortar is well understood to lead to partial hydration. On the contrary, a hydraulic lime mortar placed in a high humidity environment will fail to readily carbonate and therefore not attain its full set characteristics (Allen 2003). Uptake of lime mortar is currently low in many parts of the world, but interest is growing globally.

Although research relating to the hydration processes of lime mortar has been undertaken (Pavia 2008, Allen 2003, Ball et al. 2009, Ball et al. 2010, El-Turki et al. 2007), there are many aspects not yet sufficiently understood. The wide scale adoption of alternative binders (i.e. NHL) can only be achieved if suitable set characteristics can be attained. Uptake of NHL in extreme climate such as arid and tropical regions would be surmised to be slow due to the climatic conditions prohibiting carbonation and hydration. These negative performance characteristics would therefore reduce uptake.

The performance of hydraulic lime mortar in extreme environments has been little studied. The use of this material in these conditions and the tolerances to which they can perform requires further investigation as lime is perceived as being sensitive to climatic exposure variations during construction. Thus, this research aims to establish whether modifications of NHL's can enhance performance and therefore inadvertently stimulate wider uptake for applications associated with unfavourable environmental condition.

1.5 Hypothesis, Research Aim and Objectives

The hypothesis, research aims and objectives are established as follows;

1.5.1 Hypothesis

The incorporation of calcitic aggregate enhances the rapidity of set and positively influences the physical properties in natural hydraulic lime mortars in high temperature and humidity environments.

1.5.2 The Research Aim

The aim of the research is to undertake an analysis of the influence of calcitic aggregate modifications in natural hydraulic lime mortars and determine their subsequent effect on early strength development and other physical phenomena. This programme has ultimately been developed to aid specification of mortars in high temperature and high humidity environments such as the Tropics.

1.5.3 The Research Objectives

The research is multi-phase in nature with the objectives being based on 5 main areas;

a. to investigate the effects of hydraulic lime mortar performance exposed to high temperature and humidity during curing;
b. to investigate the effects of mortar seeding on chemical properties using laboratory testing techniques i.e. composition of binder;
c. to investigate the effects of mortar seeding on physical properties using laboratory testing techniques i.e. strength;
d. to investigate how mortar seeding additives affect the moisture handling characteristics e.g. capillary absorption;
e. to investigate micro-structural changes that arise from the incorporation of mortar seeding additives through the use of SEM analysis.

1.6 Organization of the Thesis

This thesis is organised into 7 chapters. The thesis begins by introducing the direction of this research by stating the problem associating with lime mortar use in high humidity and temperature climates. It also discusses the significance of this research within the broad context of lime mortar as a research field. Hypothesis, research and aims and objectives are clearly stated as being fundamental to this research programme.

The second chapter reviews previous literature and research on the characteristics and the testing of lime mortars with particular emphasis on the modification of naturally hydraulic lime mortars. The discussion investigates the subsequent effect on early strength development and its effects on the physical and chemical properties of lime mortars. Previous research has been incorporated into this chapter to support the possibility of the mortar modification through seeding process.

The research programme has been developed from a critical analysis of previous research in chapter 2. Chapter 3 outlines the experimental procedure, including the characterisation of the materials used in the study and details of the manufacture, curing and testing of the mortars. An experiment process flow chart is methodically presented in Figure 3.1.

Chapter 4 establishes the results of the experimental procedure. Chapter 5 critically evaluates the results and formulates the discussion of the study. The thesis concludes in chapters 6 and 7 with a summary of the findings of the study and identifies areas of potential further research that should be conducted. The thesis ends with the references and appendices.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction to Lime Mortars

Lime is a chemical compound used as a binder for the production of mortars, plasters and renders (Hughes and Valek 2003, Ashurst 2002). When lime is mixed with aggregates (e.g. sand or gravel) and water, it becomes a mortar where it can be used in a plastic state and will harden to form a relatively durable material (Gibbons and Newsom 2003). Lime has been used for many constructional purposes including foundations, walls, floors, vaults and roof and also used as building finishes for example paints, plasters (both decorative and flat work), renders and hand modelled stuccos for aesthetic aspects of building. Berge (2000) suggests that lime is the most important non-metallic material in the building industry. Holmes and Wingate (2002) reinforce the importance of lime mortar indicating that it has been proven to be very compatible with adjacent historic building materials (Forster 2010a, Forster 2010b, Forster and Douglas 2010). It has also been shown that its longevity under mechanical and environmental loads is good. For an example, the Tower of London (around 900 years old), provides further evidence of the durability of masonry materials and historic lime mortars.

2.1.1 History of Lime Mortar

The use of lime in construction began at least 10,000 years ago (Carran et al. 2012). Evidences from sites in Anatolia, Syria, Turkestan, Sinai and Jericho have revealed that lime is one of the oldest known binders in the world (Hughes and Valek 2003, Kingery et al. 1988, Gourdin and Kingery 1975, Slocombe 2012). Clay and gypsum mortars were also commonly used in ancient Egyptian construction including the pyramids. The Romans widely adopted lime mortars circa 4000 BC (Vitruvius 2013). This material was believed to have slowly replaced clay and gypsum based mortars (Lucas 2008).

The Romans were famous for using lime for waterproof linings for aqueducts and cisterns for which they also successfully improved the use of hydraulic lime mortars by combining lime and pozzolanas in masonry structures (Cowper et al. 1998). During the Romans occupation in Scotland, they introduced the use of lime mortar and plastering techniques (Hyslop et al. 2006). The Romans employed hydraulic lime and lime:pozzolan mixtures in many construction projects as they developed the technology of lime burning (Oates 1998). Roman lime mortar technologies eventually evolved into the Scottish masonry traditions that are still widespread (Mcmillan et al. 2006). It is evident that Scotland's early builders developed considerable skill in stone construction enabling complex, and durable stone structures and their associated internal and external finishes to be constructed (Maxwell 1995).

It was believed that most historic limes were non-hydraulic or only very weakly hydraulic. This is supported by the determination of the incorporation of certain additives to alter the performance characteristics of the mortars (Ellis 2001). The Roman engineer, Vitruvius (80 - 15 BC) proposed a theory that the strongest lime was produced from the hardest white limestone (Pavia and Caro 2008). This theory was refuted by John Smeaton who conducted a series of experiments during Eddystone Lighthouse construction in 1756 (Cowper et al. 1998). Many researchers such as Smeaton aimed to achieve more reliable and stronger lime mortar mixes. Smeaton proved that lime's strength does not depend on the limestone's colour and identified which limes are able to set under water (Hughes and Valek 2003).

Smeaton believed iron and manganese ('ferruginous' substances) were the source of lime's strength but some investigators still favoured the idea that it was the clay that was the principal cause of hydraulicity (Hughes and Valek 2003). In the 19th Century, Vicat (1997) progressed this work and developed the first setting tests for hydraulic lime and concluded that lime can be divided into five categories according to its hydraulic quantities; fat lime, lean lime, feebly, moderately and eminently hydraulic lime. Vicat subsequently introduced the term 'hydraulic lime' to replace the earlier term 'water lime' utilised by Smeaton (Ashurst 2002). The term 'water lime' does not enable the subtleties of sub classification required for practical production and use.

The Eddystone lighthouse project was the first time the properties of hydraulic lime were properly recognized (Blezard 1998). These results were soon followed by a range of patented mixes based on natural or artificial cements. It was found that by firing materials at higher temperatures and powdering the sintered products these early materials had similarities to early Portland cement which has been widely available since the second half of the 19th century.

2.1.2 Diminishing Practice of Lime Mortar

The significant uptake and continued use of lime and traditional masonry construction extended up to the 1920s economic crash and the two World Wars (Maxwell 2008). The pivotal difference in the periods was the significant demand for faster new construction. Whilst lime possessed many favourable characteristics it could not satisfy the rapid construction development. Lime mortars required long curing times, and exhibited relatively low early strength development relative to its competitor; Portland cement (Hughes and Valek 2003).

The Portland cement was developed and patented by Joseph Aspdin in 1824 and further advances were made by Isaac C. Johnson in 1845 (Ashurst 2002). Portland cement had relatively rapid hardening characteristic with a higher compressive strengths and was therefore considered more durable than lime (Hughes and Valek 2003, Oates 1998). Primarily due to the rapid hardening and reduced curing times, Portland cement was widely considered to be very cost effective (Neville 1996) and unlike lime, Portland cement hardened regardless of most weather conditions and wetting and drying cycles.

Portland cement as a material also resonated with changing innovations in architectural technologies and ultimately modernist styles (Yeomans 1997). Concrete buildings were designed with taller and thinner masonry walls, being built more quickly and theoretically reducing the long term obligation of costly, frequent repair interventions, e.g. re-pointing (Yates and Ferguson 2008, Mack and Speweik 1998). Reinforced concrete and precast elements developed in the late 19th century, broadening the use of concrete as a building material (Urquhart 2013).

2.1.3 Re-emerging of Lime Mortar

The decline in the demand for building lime had a corresponding decrease in the lime production capacity. The patenting of Portland cements marked the beginning of the decline of lime, and local lime kilns were abandoned as the cement industry grew (Teasdale 2005). It also caused to a gradual disappearance of the traditional skills required to both produce the high quality materials and to use it in a skilled manner associated with the artisan craft tradition (Holmes and Wingate 2002).

Unknown to these specifiers and craftsmen, problems and significant latent defects arose when Portland cement was increasingly used to repair traditional buildings that were originally built using lime mortar. The widespread use of relatively impervious materials (including Portland cement) in building conservation works caused masonry integrity problems, sustainability concerns and increased moisture entrapment (Teutonico et al. 1993). Recently, the study of lime mortar has once again become prominent with many scientists and engineers investigating performance of these materials in an historic and contemporary context (Mitchell 2007).

2.1.4 Advantages of Using Lime Mortar

Post World War 1, the Portland cement manufacturing industry was transformed into a highly developed sector. Portland cement became cheaper and more widely available. These two principle factors as associated with replacing lime mortar in construction practice (Illston et al. 2001). In an increasingly modern world, Portland cement's fast setting and hardening rates enabled developers to achieve greater rapidity in construction processes and therefore increase profits. These benefits were clearly very important but Portland cement (PC) was latterly shown to be associated with negative performance attributes. One of the most prevalent issues was the adverse affect that cement was shown to have in the acceleration of stone decay (Hughes and Valek 2003).

Mason and Hill (1999) indicate that lime has many distinct benefits but were clearly recognised for certain perceived performance deficiencies; it is a relatively weak binder; has longer setting times; and requires a higher level of skill to use it effectively. Several key advantages are associated with limes. Lime is well understood to handle moisture more effectively than PC's that are relatively impermeable (Forster 2002, Banfill and Forster 1999, Hughes et al. 2003). Lime's ability to 'breathe' plays an important role in the performance of traditionally built structures that rely upon the ready absorption and evaporation of moisture in their attempts to attain equilibrium (Hughes 1986). Conversely the modern cavity wall, built in cement mortar does not require breathability of materials to perform satisfactorily. It has been designed with drainage and impermeability of materials at its heart. Both PC and lime based materials work well when utilised for relevant methods of construction. Problems arise when relatively impermeable PC is utilised on breathable wall technologies (i.e. mass masonry built in lime). This situation has been shown to increase the incidence of moisture entrapment which can lead to decay of built in timbers and reduce material thermal properties (Hughes and Valek 2003).

Lime mortar has been shown to reduce the rate of stone decay due to its compatibility in terms of its permeability and flexibility characteristics (Hughes and Valek 2003). Ordinary Portland cement (OPC) mortars are harder, less permeable and more flexible than natural stone adopted for construction (Forsyth 2007). These negative factors can lead to spalling of materials and adverse moisture build-up.

Cement produces four times more carbon dioxide in its production cycle of which only a small fraction is reabsorbed by cement by what is generally considered to be a detrimental process. Carbonation of concrete neutralises the alkalinity which protects steel against corrosion in reinforced concrete. Lime has been shown to reabsorb CO_2 from the atmosphere as part of the setting process, and has therefore better environmental credentials (carbon neutral) (Ashurst 2002).

There are other benefits of using hydraulic lime that should be considered by those specifying mortars. Lime is both recyclable and biodegradable, the use enabling bricks to be recycled when a building reaches the end of its lifetime (Elizabeth and Adams 2005). Bricks bonded in relatively strong cement, cannot be easily recycled without causing damage to the brick. This may seem a minor point, however, it is estimated that over 100 million tonnes of material debris is buried in UK landfill sites each year and construction waste is the largest single source of waste arising in England (GB 2007). Demand for hydraulic lime mortars that offer the long-term sustainability and carbon reduction are welcomed.

2.2 Mineralogy of Limestone

The chemical components of calcium carbonate - dissolved calcium ions and carbon dioxide - are widely distributed within the earth’s crust. Limestone deposits are widely distributed throughout the world, and therefore a high proportion of humanity has ready access to the material. Calcium is the fifth most common element in the earth’s crust (after oxygen, silicon, aluminium and iron) (Oates 1998).

Boynton (1980) defines limestone as a sedimentary rock whose main mineral component is calcite or calcium carbonate ($CaCO_3$) with minor amounts of magnesium carbonate ($MgCO_3$), silica, clay, iron oxide or carbonaceous material. Hyslop et al. (2006:14) applied the more commonly used definition in their research;

> *"Limestone is a sedimentary rock principally composed of calcium and/or magnesium carbonate, commonly formed from the accumulation of fragments of marine organisms. It is widely variable in colour and texture and may contain fossils on a microscopic or macroscopic scale"*

Toprak (2007) argued that it is very difficult to find the limestone in the pure form of calcite. Different crystal forms, compositions, the characteristics of limestone vary according to the 'impurities' contained which give rise to a variety of types of lime of differing quality and characteristics (Gibbons et al. 2003). Limestone's colours may be white, cream, buff, grey or variegated patterns of all of these colours (Brantley and Brantley 1996). Colour variations depend on the impurities present such as clay constituents; and more specifically; silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3) sulphur, phosphate, alkalis etc (Boynton 1980). According to Vicat (1997), a very small quantity of iron is sufficient to change the ordinary whiteness of the lime, making it yellow, red and greenish-yellow shade. Limestone often has a musty or earthly odour, which is caused by its carbonaceous content (Oates 1998).

2.2.1 Limestone Extraction Process

Extraction (more commonly referred to as quarrying) consists of removing blocks or pieces of stone from an identified and unearthed geologic deposit (Scott and Bristow 2002). Differences in the particular quarrying techniques used often stems from variations in the physical properties of the deposit itself such as density, fracturing/bedding planes, depth, financial considerations and the site owner's preference (Modena et al. 2005).

For creating usable material, the rock is quarried, crushed, ground, washed and screened to the required size range (Lyons 2010). The techniques used in extracting limestone are similar to other hard rock where it is extracted by both surface quarrying and underground mining operations (Chamley 2003).

In surface extraction, the massive deposits that crop out at or close to the Earth's surface and extend to the depths are exploited where the top soil and other unproductive formations covering the exploited material are removed from the extraction zone (Bennett and Doyle 1997). Underground mining of limestone uses the 'room and pillar' technique. The process is relatively simple; locate or create (minimal) breaks in the stone, remove the stone using heavy machinery, secure the stone on a vehicle for transport and move the material to storage. Figure 2.1 shows the basic process of limestone extraction process;

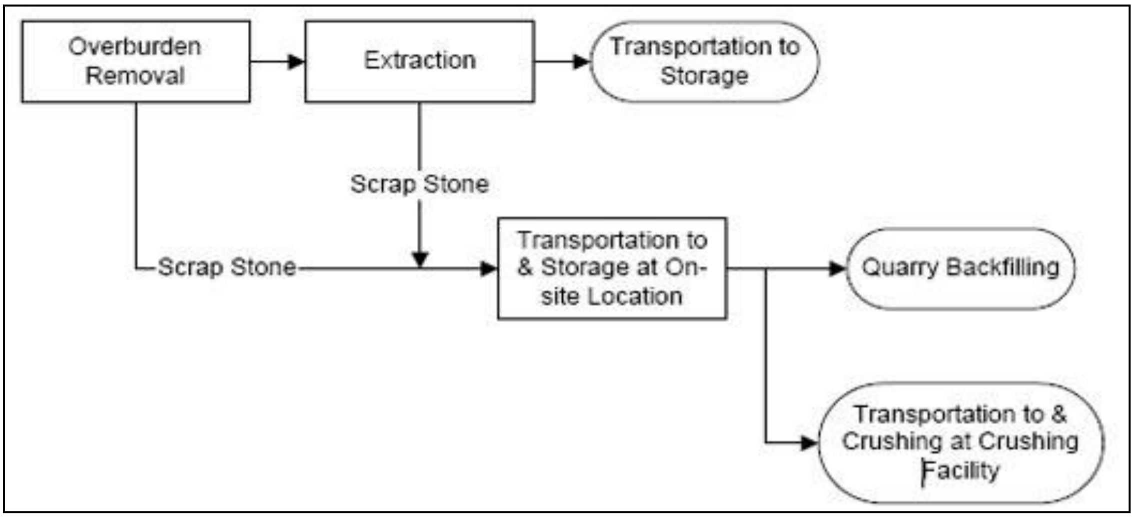


Figure 2.1: Basic Limestone Extraction Process (Oates, 1998)

As mining costs per tonne of saleable product are generally much higher than those of quarrying, there have to be special circumstances to justify operating in this way (Oates 1998). Taking into account of earlier technology, Oates (1998) concluded that mining operations were very labour intensive but the introduction of mechanisation in the late 1940's, dramatically reduced labour requirements.

In recent years, scientists have begun developing research to understand the impact of the stone extraction industry in terms of embodied energy and CO_2 footprint. It is important to understand the development of a life cycle analysis (LCA) based approach to embodied carbon accounting applied within a context of stone extraction (Crishna et al. 2011). Hammond and Jones (2008) summarises embodied energy and CO_2 values of limestone extraction in Table 2.1 based on average extraction activities in the United Kingdom and United States.

Table 2.1: Embodied energy and CO_2 values for limestone (Hammond and Jones 2008)

Research Area	Embodied energy (MJ/kg)	Embodied CO_2 ($kgCO_2/kg$)
United States	0.964	0.105
United Kingdom	0.3	0.017

Clearly, this work on natural hydraulic limes complements work by Crishna et al. 2011, Hammond and Jones (2008), and Forster et al (2011) in so much as it adds to the collective knowledge on carbon management in the built environment.

2.2.2 Calcination of Limestone

Calcination is a process in which limestone is heated below its melting temperature resulting in dissociation into carbon dioxide and calcium oxide (Kogel 2006). Calcination temperatures should be controlled very closely as overly high firing temperatures can lead to 'over-burnt' materials (Boynton 1980, Holmes and Wingate 2002). To achieve relatively even temperature, Hassibi (1999) suggested that the particle size of limestone must be small, typically about 40mm to avoid long residence time in the kiln.

Theoretically, the raw limestone is calcined (raised to elevated temperature below its melting point) in a lime kiln to approximately 850°C (Gibbons et al. 2003). Holmes and Wingate (2002) argued that the calcination temperature should be 900°C taking into consideration on the limestone size, type of kiln and type of fuel used. Hassibi (1999) claims that the temperature should to be approximately 1350°C but this statement was refuted by Ashurst et al. (2002).

Quicklime is significantly lighter (approximately half the weight) than the limestone from which it has produced due to loss of CO_2 (Holmes and Wingate 2002). As the temperature rises, approaching white heat (900 - 1200°C), the carbonates begin to decompose and 'give up' their carbon dioxide (Cowper et al. 1998). When outer layer of limestone is heated to dissociation temperature, the carbon dioxide (CO_2) escapes the stone, leaving capillary passages that increase the porosity of the calcium oxide (quicklime) (Gibbons et al. 2003).

Figure 2.2 (Hassibi 1999) diagrammatically illustrates the calcination process with the interrelationship of heat, and CO_2 dissociation. It highlights that if an overly large piece of stone or insufficient residence time is adopted then an un-burnt core can result. This centre core is sometimes referred to as 'grit'. Conversely in medium sized and smaller stones if the calcinations process is overly long, sintering of the outer layers can form a hard outer shell that water cannot penetrate. These 'over-burnt' materials are clearly problematic.

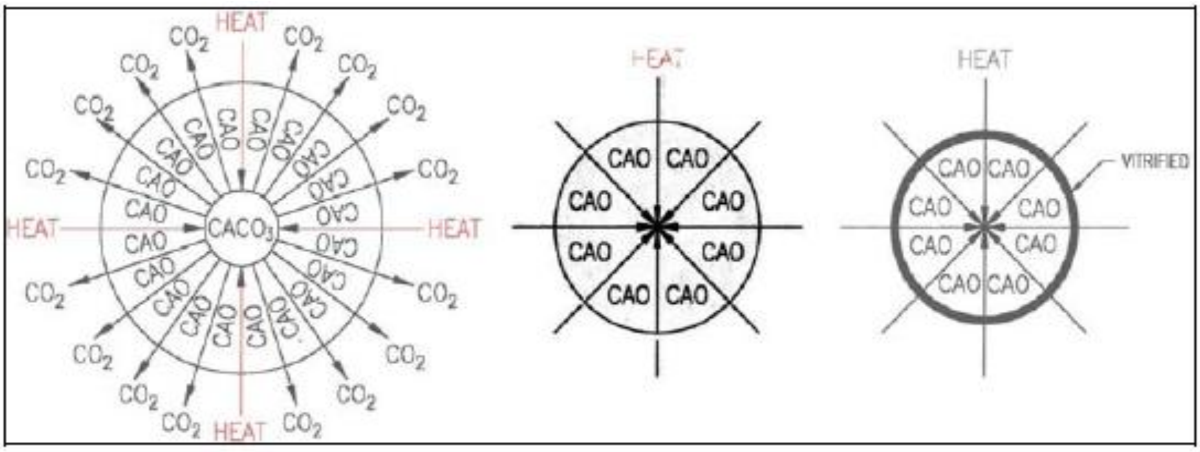


Figure 2.2: Transformation of Calcium Carbonate to Calcium Oxide Due to Heat Penetration during Calcination (Hassibi 1999)

Correct temperature and residence time during calcination both influence the quality of CaO produced. This directly influences the limes reactivity (Forster 2004a, Forster 2004b). Hassibi (1999) suggests that the most common problem associated with a calcination process is over-burned lime. The over-burned quicklime feels denser and may have a sintered surface (Holmes and Wingate 2002). It may also be associeted with the production of clinker (grappiers) similar to Portland cement. These are relatively inactive until very finely ground (Wingate et al. 1985). Over-burned quicklime will resulting late hydration and Hassibi (1999) suggests that these materials require vigorous agitation to break the hardend outer layer of the calcium oxide to open up the pores enabling water to penetrate.

Under-burned quicklime (limestone that burned at too low temperature or too short a period of residence time) will also influence the reactivity (Forster 2004b). This type of quicklime contains a residual core of converted or only partial of the material converted carbonate resulting a relatively heavy material because of its denser core (Holmes and Wingate 2002). According to Holmes and Wingate (2002), this type of quicklime can often be seen in old mortar when the efficiency of calcination process is less efficient.

2.2.3 Process Subsitution

Meier (2005) suggests that by substituting concentrated solar energy in place of the fossil fuels used in the calcination process could reduce the carbon dioxide emissions in a modern lime plant by 20% and in a conventional cement plant by 40%. Mahasenan (2005) suggests various strategies for achieving effeciencies; including using better process control systems, making process improvements and converting more energy-efficient processes. A tangible example would be to switch to fuels with a lower carbon content (e.g. from coal to natural gas) or by using fuels that qualify for an emissions credit (e.g. biomass and waste tires) (Azar et al. 2006). Mahasenan (2005) emphasises that the selection of carbon dioxide reduction strategies must be evaluated based on existing capital stock, future demand, investment cost and climate change.

2.3 Classifications of Lime Mortars

The classification of limes is usually based on the proportions of the mineralogical composition and the nature of calcination (the amount of calcium oxide, magnesium oxide and argillaceous matter). The hydraulicity of quicklime reflects its relative reactivity during slaking with a non hydraulic material having the greater affinity for water (Cowper et al. 1998).

2.3.1 Early Classification

Bergoin (1998) indicates that the lime classification initially suggested by Vicat based on slaking reactivity test results and by chemical analysis of elemental components was used for traditional classification (see Table 2.2). In Vicat's chemical analysis, magnesium lime showed the least degree of expansion in his slaking test (Cowper et al. 1998).

Table 2.2: Lime Classification According to Vicat (Cowper et al. 1998)

Classification	Lime
Class A	Rich or fat lime
Class B	Poor or lean lime
Class C 1	Feebly hydraulic lime
Class C 2	Moderately hydraulic lime
Class C 3	Eminently hydraulic lime

Limes can be categorised into two principal types; (i) hydraulic and (ii) non-hydraulic (see Figure 2.3). Non-hydraulic lime is classified according to its calcium and magnesium oxide contents and hydraulic lime is classified according to its compressive strength and the ability to undergo chemical set even with presence of water. Hydraulic lime has specific proportions of minerals such as clay or any other reactive forms of silicates and aluminates such as calcium silicates, calcium aluminates and/or alumina-silicates and calcium oxide (Vicat 1997, Lyons 2010, Vicat and Wingate 1997, Forster 2004b, Forster 2004c).

British Standards establish the formal classification relating to the quality and performance of lime mortars. They standardised laboratory testing for new materials but do not cover or reflect the complexity of historic or traditional mortars (Hughes and Valek 2003). The earlier version, BS 890: 1995 - Specification for Building Limes was used but it has now withdrawn to be replaced by;

a. BS EN 459-1: 2010 Building lime. Definitions, specifications and conformity criteria;
b. BS EN 459-2: 2010 Building lime. Test methods;
c. BS EN 459-3: 2011 Conformity evaluation.

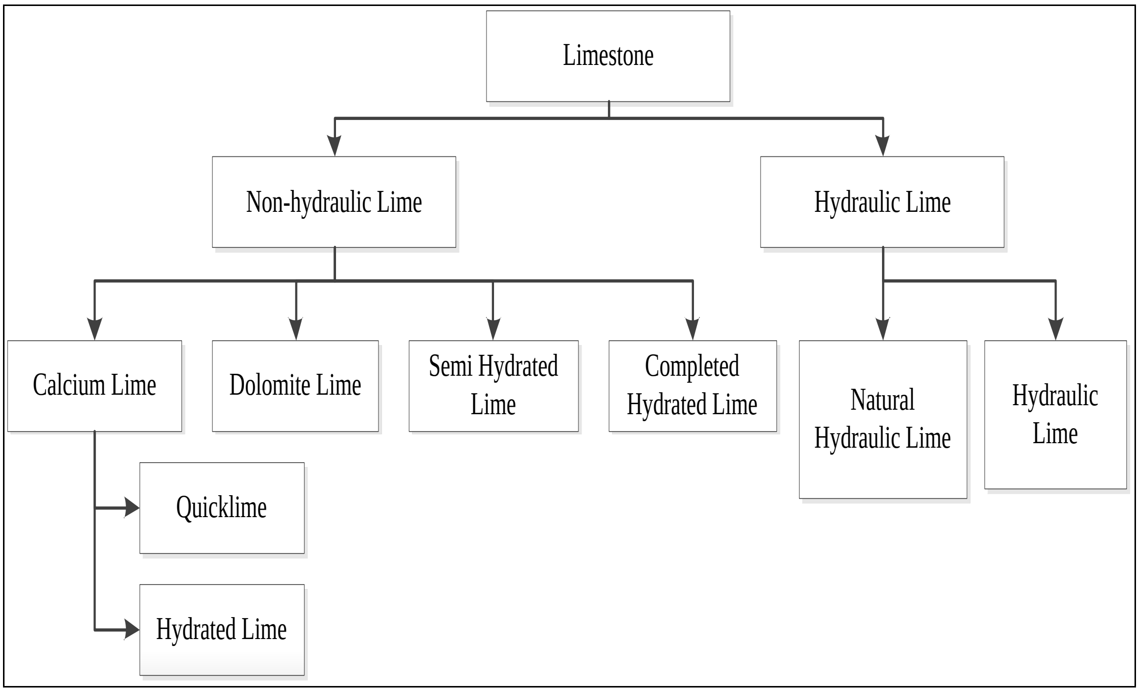


Figure 2.3: Types of building lime (Lyons 2010)

2.3.2 Non-hydraulic Lime

Non-hydraulic lime (aka fat lime) in its purest form is defined as a type of limestone contains more than 90% calcium carbonate and potentially as high as 98% calcium carbonate (Mason and Hill 1999). Non-hydraulic limes are derived from limestones that do not contain clay. The most reactive non-hydraulic lime is made from limestone containing very high proportion of calcium carbonate such as chalk and talc tufa (Gibbons and Newsom 2003). Non-hydraulic limes rely upon CO_2 for their setting and hardening process known as ‘carbonation’ (Holmes and Wingate 2002).

When quicklime is combined with water in the slaking process, it becomes calcium hydroxide ($Ca(OH)_2$) or hydrated lime. The slaking process is synonymous with the materials reactivity with water. Key to this is a very vigorous exothermic reaction which releases a great quantity of heat (Hassibi 1999). Hydration results in the conversion of calcium oxide into calcium hydroxide. This can be produced as fine powder called hydrated or slaked lime. Hydrated lime is much safer and a more convenient material to handle and use than quicklime (Mason and Hill 1999). It is usually sold in the form of a dry powder or can also be prepared as lime putty depending on the suitability of the usage purposes (Holmes and Wingate 2002).

When the non hydraulic hydrated lime is used as mortar it sets through the integration of moisture and CO_2 from the atmosphere, reforming calcium carbonate ($CaCO_3$). This process is called carbonation. It is an excellent material used to great effect with stones or bricks and acts in a sacrificial manner protecting the host masonry. The sequence of chemical changes involved in the production and curing of pure lime is frequently referred to lime cycle as shown in Figure 2.4 and Figure 2.6 (Gibbons and Newsom 2003).

2.3.3 Non-hydraulic Lime Cycle

The lime cycle (Figure 2.4) illustrates the complex process of converting limestone into a final set mortar. It explains the creation of quicklime after heating, its conversion into hydrated lime (slaked lime or calcium hydroxide) after adding water and finally, and its carbonation, reverting back into limestone after it reacts with carbon dioxide from the air.

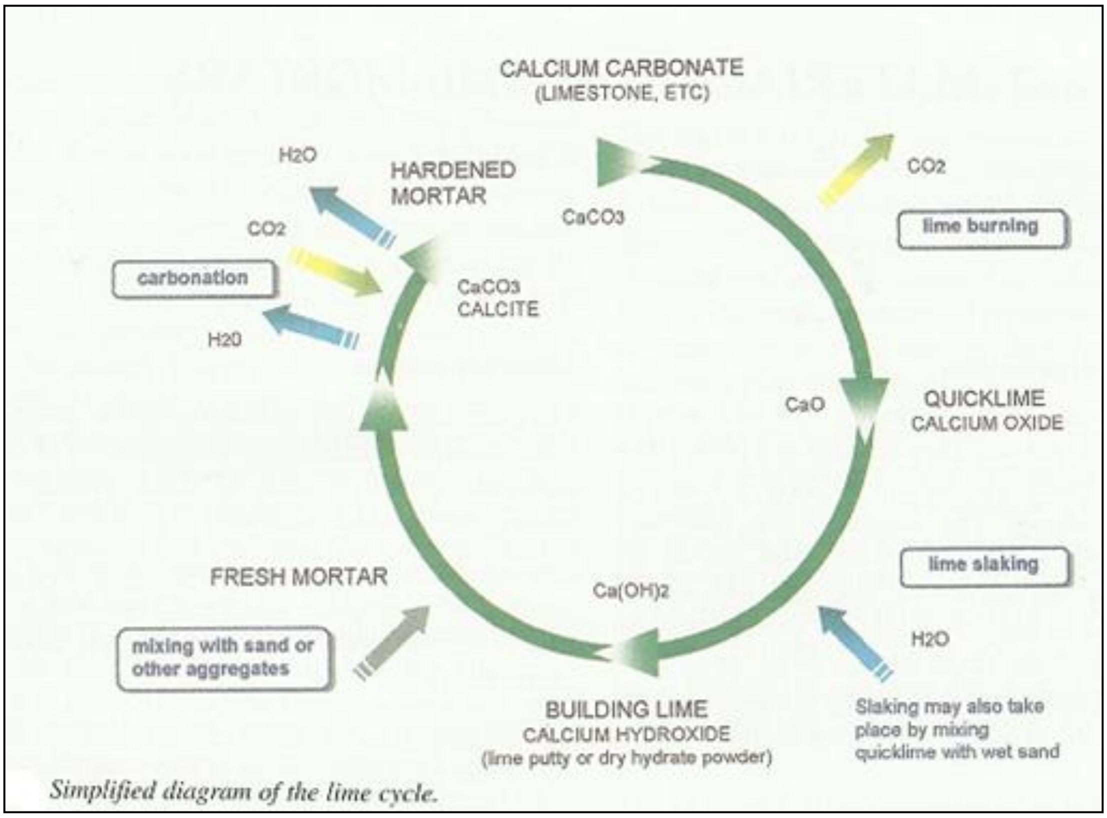


Figure 2.4: Lime cycle (Gibbons and Newsom 2003)

An appreciation of the compressive strength of a mortar provides information on its structural resistance (Charola and Henriques 1999). The compressive strength of a fat lime (high calcium lime) mortar immediately after manufacture is governed by the water content. As the mortar dehydrates, the compressive strength increases (Lawrence 2006). According to Vicat (1997), fat lime mortar has little strength prior to setting. Upon carbonation low level mechanical strength ensues. Forster (2004b) highlights in his work that fat lime (with 100% degree of carbonation) has only 2-3 N/mm^2 of compressive strength. Historically Vicat recognised the deficiency of fat lime in so much that it cannot be used in thick brick walls or masonry because it has no considerable strength without adding any pozzolan additives (Cowper et al. 1998). Chandra (2003: page 434) defines non-hydraulic lime mortar setting process as;

> *"The hardening of common lime mortar is due to the formation of a carbonate of lime by the absorption from the atmosphere of carbon dioxide. This will penetrate for a considerable depth in course of time; but instance are common in which masonry has been torn down after having been erected many years, and the lime mortar in the interior has found still soft and unset, since it was hermetically cut off from the carbon dioxide of the atmosphere. For the same reason, common lime mortar will not be harden under water, and therefore it is*

> *utterly useless to employ it for work under water or for large masses of masonry"*

2.3.4 Carbonation

Carbonation is the result of the dissolution of carbon dioxide in the concrete pore fluid and this reacts with calcium from calcium hydroxide (alkaline) to form calcite ($CaCO_3$) (neutral). The carbonation process in lime mortar is influenced by the diffusion of carbon dioxide into the mortar pore system, and by the drying and wetting process in the mortar (Van Balen 2005). Carbonation is fundamental in the development of lime mortars and therefore their long term durability (Lawrence 2006).

Carbonation occurs in all lime mortar; both, non-hydraulic and hydraulic lime mortars (Forster 2004b, Forster 2004c). The carbonation reaction is important for the development of compressive strength and is normally a slow process (Taylor 1997). A non-hydraulic lime mortar derives all its mechanical strength due to this reaction (Holmes and Wingate 2002).

A lime mortar hardens principally by its conversion from calcium hydroxide to crystalline calcium carbonate (Ashurst 2002). For the carbonation process to occur the mortar must be accessible to air (atmospheric carbon dioxide) and the presence of water is essential. This is required to enable the dissolution of carbon dioxide into the pore water forming carbonic acid. Lawrence (2006) established five stages of carbonation phase as shown in Figure 2.5.

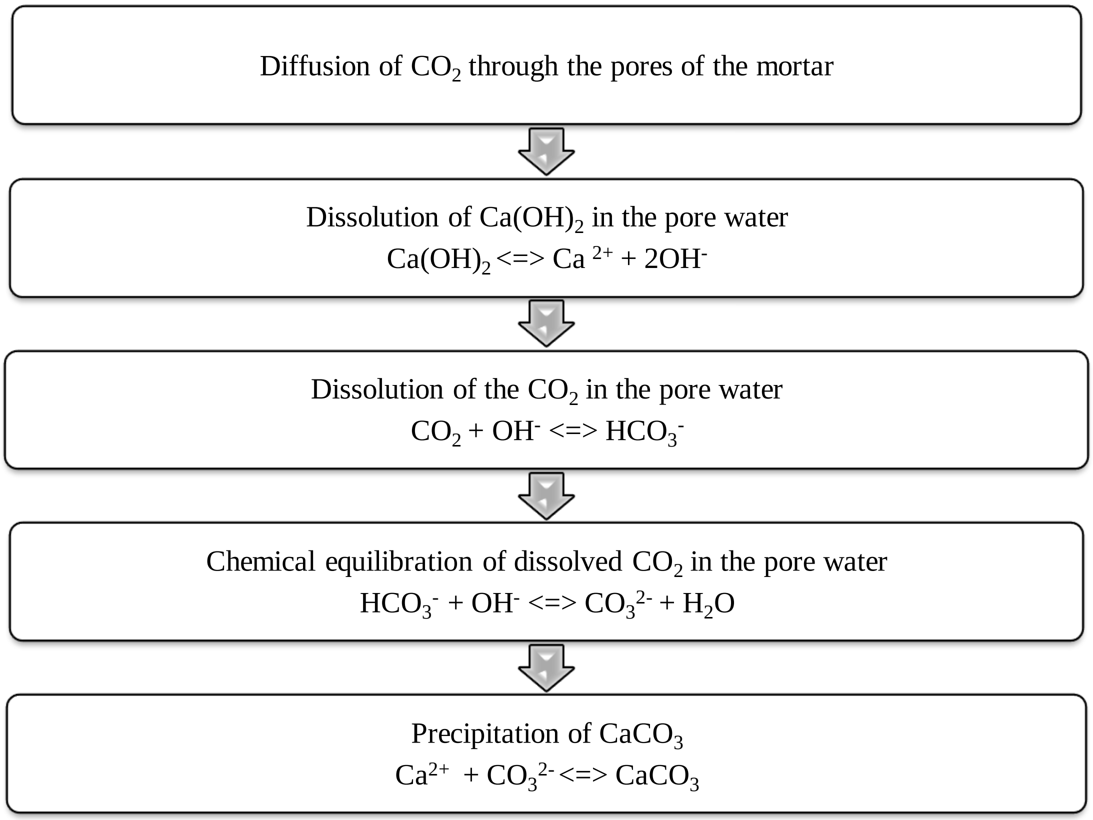


Figure 2.5: Five Phase of Carbonation Process in Lime Mortar (Lawrence, 2006)

Practically, calcium hydroxide will be carried to the surface of mortar by moisture migrating through the material. This is called laitance (Hageman 2008, Torney 2013, Frew 2007). The lime is deposited on the surface as the water evaporates, and the lime combines with carbon dioxide (CO_2) in the atmosphere to form calcium carbonate ($CaCO_3$). This is sometimes seen on the surface of mortar or masonry as a white chalky deposit or a greyish-brown film in the surface (Forster 2007, Forster and Szadurski 2012). The same conversion of lime to calcium carbonate lowers its alkalinity.

2.3.5 Variables Influencing the Carbonation Process

This process depends on many variables such as relative humidity, temperature and carbon dioxide diffusivity and normally involves an increase in mass caused by the transformation of portlandite into calcite (Dheilly et al. 2002). Until carbonation has been fully completed, the mortar cannot be considered to have attained its full potential (Lawrence 2006). The extent of carbonation, clearly, depends on the aforementioned factors and it has been suggested that the total carbonation of mortar could take centuries (Torney et al. 2014)

2.3.5.1 Carbon Dioxide Diffusivity

Carbon dioxide must be reactive in order to achieve an effective carbonation. The carbonation process is slow, as it is controlled by the diffusion of carbon dioxide into the mortar (Lyons 2010). Diffusivity of carbon dioxide is constrained by the physical properties of the solid i.e. compaction pressure and exposure conditions (Bertos et al. 2004). The higher the quantity of carbon dioxide in the gas phase, the higher the rate of carbonation. However, excess carbon dioxide pressure does not lead to a higher strength of carbonated product (slower reaction would allow for dissipation of heat and reduce stresses on the product) (Lange et al. 1996). The rate of carbonation depends on moisture content of the material and occurs very quickly on the outer surface, especially in a saturated CO_2 atmosphere (Van Balen and Van Gemert 1994). The mortar depth also influences the carbonation level (Lawrence 2006).

2.3.5.2 Porosity

Carbonation of OPC concrete materials is well understood. It is a significant defect in concrete and is generally associated with high porosity materials. The diffusivity of carbon dioxide depends upon the pore system of hardened mortar and the exposure condition (Jianga et al. 2000, Song et al. 2006). The pore system of hardened mortar depends upon water/binder ratio, type of binder and degree of hydration.

Study by Al-Khaiat et al. (2004) suggested the water/binder ratio is one of the main factors affecting carbonation which the values of sorptivity, k ranged from 2.1 to 7.8 mm/year$^{0.5}$ as the water/cement ratio increased from 0.45 to 0.8 mm/year$^{0.5}$ (sorptivity, 'k' was applied as a constant for the carbonation reaction). Carbonation occurs progressively from the outside of concrete exposed to carbon dioxide. The rate is slow due to the carbon dioxide’s difficulty in diffusing through the relatively dense pore system, including the already carbonated surface zone of mortar (Bertos et al. 2004).

The carbonation of lime mortars must be considered differently, as unlike OPC it is clearly a desired property. These mortars and their ability to clearly carbonate are still influenced by the relative porosity of the materials aiding CO_2 diffusion. Modification of the materials can aid the carbonation process. For example, when the sand or stone aggregates is added to the lime putty to form a mortar, the increased porosity allows greater access of carbon dioxide and a speeder carbonation process.

2.3.5.3 Temperature and Humidity

According to Ashurst (2002), carbonation does not always occur consistently and is moisture and temperature dependent. Allen et al. (2003) indicates that the mortar constituents heavily influenced the carbonation rate (see Table 2.3). In addition, more permeable are more readily to carbonates due to the open textured surfaces that encourage diffusivity enabling greater depth of penetration. Conversely, smooth or heavily over worked finishes have been shown to reduce this process.

Table 2.3: Carbonation rates for mortars exposed to 20°C - 90% RH (Allen et al. 2003)

Rate of carbonation	Mortars
Very High	CL 90
High	NHL 2 1:2 NHL 2 1:3 NHL 3.5 1:4 NHL 3.5 1:6 CL 90 + 10% metakolin
Moderate	NHL 3.5 1:2½ NHL 3.5 1:3 NHL 3.5 1:3 brick dust, natural pozzolona NHL 5 1:4 CL90 + 30% metakolin
Low	NHL 3.5 1:1 NHL 3.5 1:3 NHL 3.5 1:2 NHL 3.5 1:3 + 10% putty NHL 3.5 1:3 + 50% CL 90 NHL 3.5 1:3 + slag, fly ash, metakolin, micro silica NHL 5 1:2 NHL 5 1:3
Very Low	OPC:CL 90 1:1:6 and 1:2:9 and masonry cement 1:4

Lime mortar specimens carbonate most quickly in damp (high relative humidity) but not in saturated condition. This is because excessive humidity hinders gas diffusion based on empirical equation (see Equation 2.1) by Steffens et al. (2002);

$$f_{\mathrm{H}} = a_1 + \frac{a_2}{1 + (a_3 - \ a_{3\phi})^{a4}}$$

(Equation 2.1)

In which the parameters were identified as ϕ = humidity, a_1= 0.993, a_2= −0.974, a_3= 3.621 and a_4= 5.750. This function is shown in Figure 2.6;

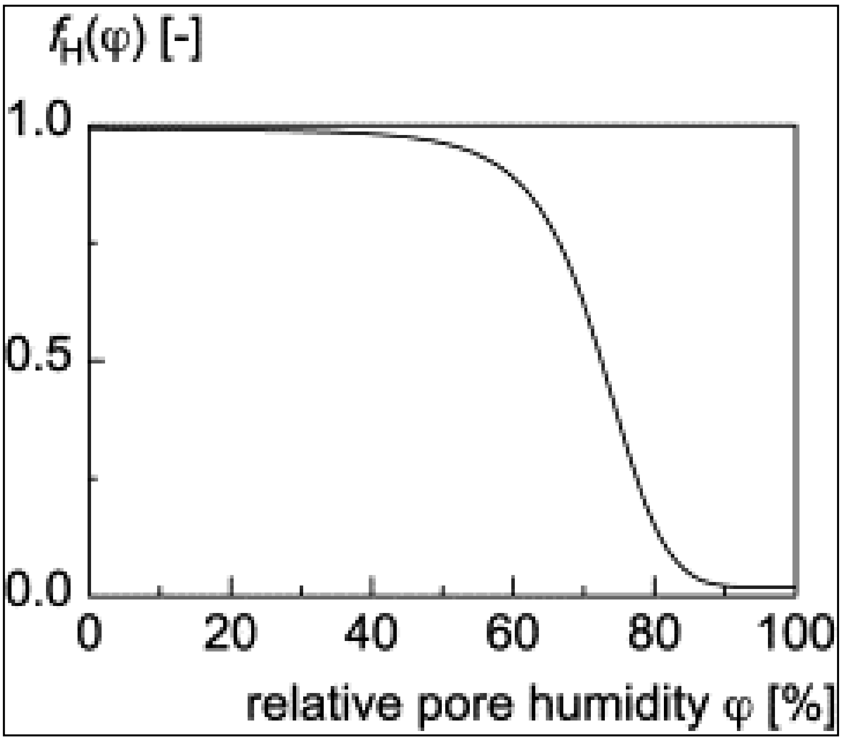


Figure 2.6: Humidity effect on diffusion coefficient of CO_2 (Steffens et al. 2002)

When saturated, a mortar cannot readily carbonate except via the very much slower means of liquid diffusion (Ball et al. 2010, Ball et al. 2009). Specimens in dry or saturated conditions carbonated slowly, if at all. Hence a low relative humidity environment will inhibit carbonation (Allen et al. 2003). Carbonation cannot occur in low relative humidity since there is insufficient pore water present for either calcium hydroxide or carbon dioxide to dissolve into (Lawrence 2006).

Moorehead (1986) indicates that when the carbon dioxide gas temperature increases, the reaction rate decreases. This is due to the solubility of carbon dioxide in water which decreases to one quarter if the temperature is raised from 15°C to 60°C.

Rapid drying which sometimes takes place in hot weather on unprotected work can impede the carbonation process resulting in poor ultimate strength (Ashurst 2002). Conversely, wet lime putties will not carbonate if they are kept sealed from the air enabling them to be stored indefinitely.

2.3.6 Un-carbonated Mortar

It has been shown that after the apparent full carbonation of lime has occurred, there are still small quantities of un-carbonated Portlandite present (Lawrence 2006). It is very useful to know how rapidly and to what extent each mortar carbonates. The extent of carbonation varies according to the distance from the exterior, and as Lawrence (2006) suggested it is useful to examine the shape of a mortars carbonation profile as this relates directly to the strength of the mortar.

2.3.7 Measuring Carbonation Depth

Carbonation is the result of the dissolution of carbon dioxide in the mortar pore fluid and this reacts with calcium from calcium hydroxide to form calcite ($CaCO_3$) (Rozière et al. 2009). Additionally, calcium hydroxide is produced in the hydration reaction associated with Belite (C_2S). Aragonite may form in hot conditions (Prabhakar et al. 2013). Fresh mortar paste has a pH of about 13. Carbonation of the mortar has the effect of reducing the pH.

Carbonation depth is assessed using a solution of phenolphthalein indicator that appears pink when in contact with alkaline materials (pH values in excess of 9). The stain is colourless at lower pH levels (Evangelista and de Brito 2010). The test is most commonly carried out by spraying the indicator on freshly exposed surfaces of concrete and lime.

2.4 Natural Hydraulic Lime (NHL)

Natural hydraulic lime (NHL) is produced from limestone that contains clay or other impurities. When these are fired at specific temperature they form reactive calcium silicates, calcium aluminates and/or alumina-silicates and calcium oxide (Vicat 1997). These compounds are hydraulic in nature and when hydrated form relatively stable products of hydration. Teutonico et al. (1997: page 6) explains this as;

> *Hydraulic lime sets by chemical reaction with water and so differs from non-hydraulic lime, which hardens by reaction with carbon dioxide in the air. Thus hydraulic lime is capable of setting and hardening under water. The raw material for hydraulic limes is limestone, but limestone which naturally contains a proportion of clay……. Such limestone is known as argillaceous limestone and will yield hydraulic lime of varying characteristics after calcination (burning).*

2.4.1 Types of Hydraulic Lime Mortar

There are numerous types of limestone with varying mineralogical compositions with the natural stone (Hyslop et al. 2006). Grey coloured argillaceous limestone containing alumina-siliceous materials such as clay minerals are stronger than ‘fat lime’ but are not as strong as Portland cement even though they are both hydraulic (Mason and Hill 1999). Impure lime stones frequently contain other minerals which make them less suitable for lime manufacture due to a relative reduction in the percentage of calcium carbonate. This affects the availability of lime in the final product (Ashurst 2002, Gibbons et al. 2003).

Hydraulic lime are generally considered as being more durable than non-hydraulic binders and this is reflected in mortar durability classifications developed by Allen et al. (2003). This system correlates construction process, exposure and durability and highlights the difference hydraulicity and mix proportions make to performance.

2.4.2 Hydraulic Lime Cycle

The sequence of chemical changes of natural hydraulic lime has certain similarities with pure lime binders. It must however be emphasised that the hydraulic lime cycle has a greater complexity compared with non hydraulic materials (Gibbons et al. 2003). Hydraulic lime binders rely upon dual set mechanisms, namely; i) carbonation and ii) hydraulic reactivity. A hydraulic set is the chemical combination of lime, burnt clay or other pozzolanic material and water to form stable compound, even under water (Forster 2004b, Forster 2004c). Figure 2.7 illustrates the hydraulic lime cycle. The hydraulic reaction is principally composed of the dissolution of relatively soluble calcium silicate, precipitating from the liquid phase to form hydrates known as calcium silicate hydrates (C-S-H). The degree of hydraulic limes hydraulicity is influenced by the degree of impurities contained with the lime stone, the firing temperature and resonance time.

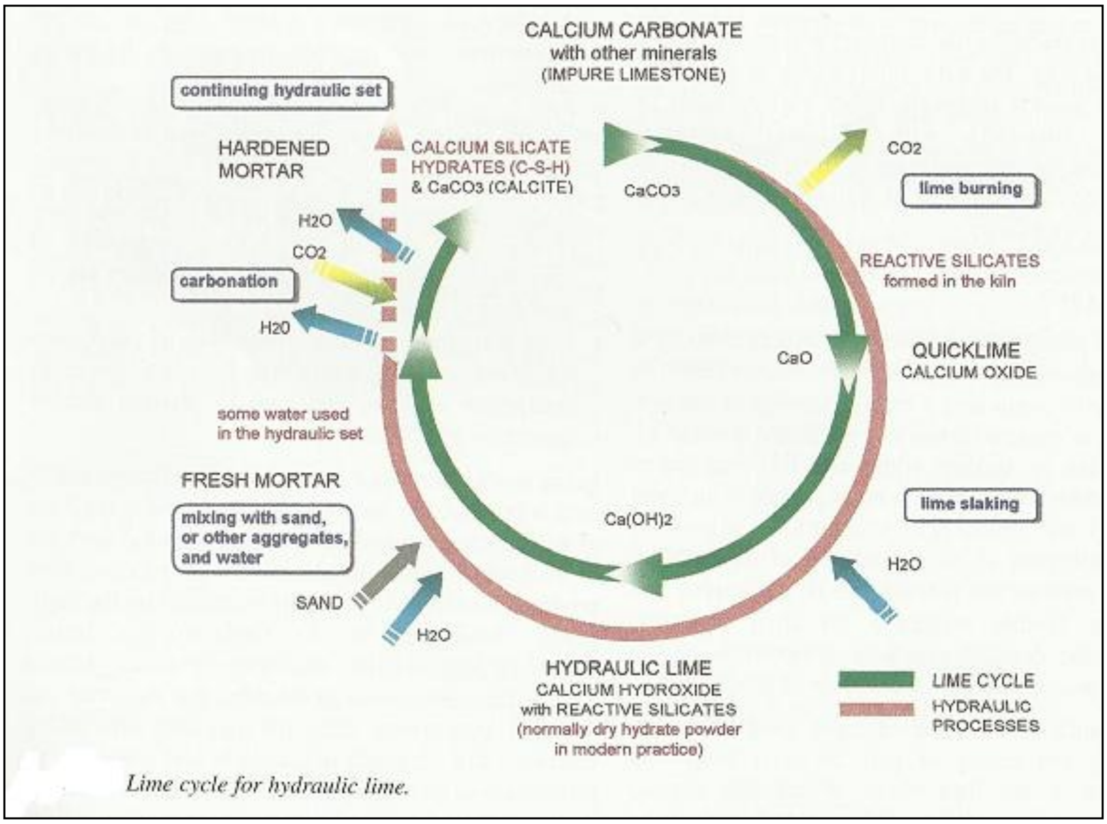


Figure 2.7: Lime cycle for hydraulic lime (Gibbons and Newsom 2003)

2.5 Hydration

2.5.1 Definition

Hydration is defined as a reaction of an anhydrous (without water) compound with water to yield a new compound named hydrates (Vicat and Wingate 1997). In cement chemistry, it is a reaction of non-hydrated cement with water, associated with both chemical and physic-mechanical changes of the system, in particular with setting and hardening (Odler 2006).

2.5.2 Process

Setting is the stiffening of the mortar after it has been placed and is characterised by a sudden loss of plasticity. A 'set' mortar is no longer workable, but will not have generally achieved sufficient strength development for practical purposes. Setting is due to early-stage calcium silicate hydrate formation and to ettringite formation. On the contrary, hardening is the longer term process of strength development and that may continue for weeks or months after the mortar has been mixed and placed. Hardening is due largely to the formation of calcium silicate hydrate as the binder continues to hydrate.

2.5.3 Reactive Compounds

Cement in its anhydrous state has four main types of reactive compounds present; alite (C_3S), belite (C_2S), tri-calcium aluminate (C_3A) and tetra-calcium alumino ferrite (C_4AF). The hydrated compounds will yield C-S-H and C-A-H. Generally, the calcined lime is hydrated with sufficient amount of water to convert the free calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) (Oates 1998). This involves many different reactions, often occurring at the same time. When water is added, the reactions are mostly exothermic (generate heat) and these compounds being classified into groups according to the primary hydrated form; calcium silicates hydrate (C-S-H) and calcium aluminates hydrates (C-A-H) (Forster 2004b, Forster 2004c).

Belite (C_2S) would hydrate into jennite-based C-S-H (the main cementing component in hydraulic lime). Calcium silicate hydrate (C-S-H) is the main reaction product and is the main source of natural hydraulic lime strength. C_3A leads to the rapid formation of C-A-H, when in the presence of water. It is a secondary component in OPC and causes rapid set which must be controlled by the addition of gypsum ($CaSO_4$) which results in the formation of ettringite and varies in concentration in hydraulic limes depending on the concentration of aluminium present and the calcination processes to which it is subjected.

In some lime mortars, ettringite is present as rod-like crystals in the early stages of reaction or sometimes as massive growths filling pores or cracks in mature concrete or mortar. In a concrete made from cement containing just clinker and gypsum, ettringite forms early on in the hydration process, but gradually replaced by monosulfate. Forster (2004b) identified the common hydraulic compounds found in Portland cement and Natural Hydraulic Lime as shown in Table 2.4.

Table 2.4: Common Compounds in Hydraulic Lime and OPC (Forster 2004b)

Clinker / Compound	**Reaction Product**	**Binders**
Alite (C_3S)	C-S-H	Cement
Belite (C_2S)	C-S-H	Hydraulic Lime & Cement
Tricalcium aluminate (C_3A)	C-A-H	Some Hydraulic Limes & Cement
Brownmillerite (C_4AF)	C-A-H	Some Hydraulic Limes & Cement
Portlandite ($Ca(OH)_2$)	Calcite ($CaCO_3$) - on carbonation	Hydraulic Lime
Calcium Oxide CaO – Portlandite ($Ca(OH)_2$)	$Ca(OH)_2$	Cement

Hydration of cement leads to the development of amorphous and crystalline products of hydration that bond the individual sand particles together. This is known as the ‘matrix’ (Valek and Matas 2012, Cultrone et al. 2005). Many factors influence the progression of hydration (Odler 2006). These include;

a. the phase composition of the cement and the presence of foreign ions within the crystalline lattices of the individual clinker phases;
b. the fineness of the cement, in particular by its particle size distribution and specific surface;
c. the water-cement ratio used;
d. the curing temperature;
e. the presence of chemical admixtures, i.e. chemical substances added in small amounts to modify the hydration rate and properties of the cement paste;
f. the presence of additives, i.e. materials inter-ground with cement in larger amounts, such as granulated blast furnace slag or pulverised fly ash.

2.5.4 Temperature Effects on Hydration

The curing temperature is known to play significant role in hydration, microstructure formation and bulk properties of mortar. Increased temperature is well understood to promote hydration leading to a high early strength development. In the later stages of curing, however, the strength of cement hydrated at increased temperature can be lower than that of equivalent samples hydrated in the room temperature. In a study which set out to determine temperature effects on cement hydration, Wang (2012) found that the evolution of hydrated phases at 60°C causes microstructure changes, reducing the final performance of the cement. Recent studies by Soriano et al. (2013) showed a reduction in the curing temperature (from 20°C and below) caused a decrease in the early stage mechanical strength and this value increases slowly for longer curing periods. Both studies found that, an inclusion of additives could lessen the adverse effects of curing temperatures.

The influences of temperature on hydration and carbonation reactions are clearly important. Practically, special techniques are used for curing mortar during extremely cold or hot weather to protect the mortar. The longer the mortar is kept moist during warm climatic conditions the better the chance of obviating rapid moisture loss and the potential for partial hydration. The rate of hardening depends upon the composition and fineness of the lime, the mix proportions, and the moisture and temperature conditions

(Allen 2003). Most of the hydration and strength gain take place within the first month of mortar's life, but it must be emphasised that hydration continues at a slower rate for many years gaining strength accumulatively (Hughes and Valek 2003).

If mortar is subjected to heat, a number of transformations and reactions occur, even if there is only a moderate increase in temperature. Several studies investigating on strength loss due to high temperature have been carried out on concrete (Chan et al. 1999, Behnood and Ziari 2008, Tanyildizi and Coskun 2008, Uysala and Tanyildizi 2012). The studies concluded that an increase in temperature produces significant changes in the chemical composition and microstructure of the hardened Portland cement paste. Aggregate materials may undergo crystal transformations leading to significant increases in volume. Naus (2005) reported findings by Harmathy and Berndt (1966) and highlighted strength loss of concrete from the elevated temperature exposure in his work. This is because, apart from the crystalline transformations occurring mainly in the aggregate materials during heating, a number of degradation reactions occur, primarily in the cement paste, that result in a progressive breakdown in the structure of the concrete.

The development of hydration is associated with the liberation of heat. The degree of heat relates to the relative properties of hydraulic reactive compounds in the material. The intensity of heat liberated over time depends on the type of chemical, surface area and reactivity (Mostafa and Brown 2005). The measurement of total heat and rate of heat development informs us of the hydration kinetics, degree of hydration, mechanism of hydration, the effects of additives and setting occurrence (Ramachandran 1995). Conduction calorimetry is one technique that measures the solubility hydration reaction (Ramachandran et al. 2002, Hewlett 2004). It has been established by Rojas and Cabrera (2002) that a different trend of hydration rate is encountered as the temperature increases. In their research, the amount of transformed lime at 60 °C is approximately 65% higher than that at 20 °C (see Figure 2.8).

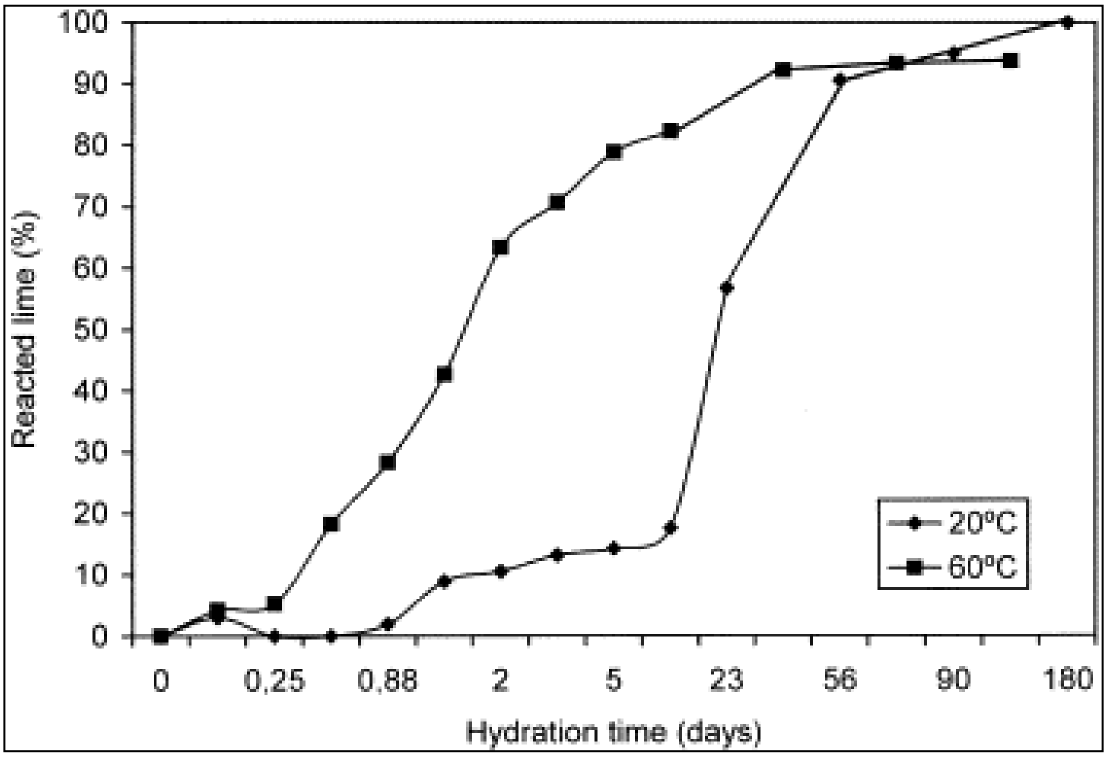


Figure 2.8: Evolution of reacted lime with curing time at different temperatures (Rojas and Cabrera 2002). The amount of total calcium hydroxide present in the mixture was calculated from the weight loss due to the dehydroxilation of $Ca(OH)_2$ (at about 400–500 °C) and decarbonation of $CaCO_3$ (at about 600–750 °C).

2.5.5 Partial Hydration

Many variables affect the hydration of lime mortar such as fineness, chemical composition of mortar, temperature and relative humidity of mixing and curing conditions (Garcia and Sharp 1998). The strength and microstructure of concrete and mortar are known to be affected by premature drying processes.

In his study on concrete, Kanna et al. (1998) found that the mechanical properties of a cement-based material at any age are generally a function of its moisture content. The removal of significant amounts of water from mortar before final set as a result of insufficient curing results in inferior properties and poor performance.

The setting process relies on repeated dissolving and precipitation of minerals within the wet mortar. It is essential to ensure that sufficient water is also present for a long enough periods to allow the hydraulic reaction to continue after the mortar has been placed. If the water evaporates too rapidly then a partially hydrated product will result. The retardation of the progress of hydration will yield a binder with poor mechanical properties (Odler 2006). If the mortar dehydrates too quickly, hydration and carbonation will be inhibited. Additionally, drying shrinkage may occur and the mortar may become friable. Partial hydration of the mortar creates a finer pore structure and inhibits carbonation process afterwards.

A high water loss from the mortar may cause unfavourable hydration conditions (Groot and Larbi 1999). Loss of water will also cause the mortar to shrink, creating tensile stresses within the concrete matrix. If these stresses develop before the mortar has attained enough strength, surface cracking can result. This is also exhibited in the aggregate interface adversely affecting the mortar / masonry bond strength (Al-Defai 2013).

2.6 Hydraulicity

2.6.1 Definition

Hydraulicity is defined as “the ability to harden under water”. This is opposed to a carbonation set (Banfill and Forster 1999). Hydraulic properties are produced by burning limestone containing silica, alumina and iron oxides above a certain temperature. The resulting silicates, aluminates and ferrites combine with calcium (Ca) yielding hydraulic properties in the product. According to Oates (1998), the degree to which this reactivity is conferred depends on the quantity of impurities present in the stone. Depending on the factors such as amount of clays present, burning temperature and time at temperature, modify the degree of reactivity. This influences the nature of the product (Charola and Henriques 1999).

2.6.2 Process

The formation of calcium silicates results due to compounding of elemental oxides. The activation of reactivity is synonymous with the conferment of solubility in the silica. A complex series of hydration reactions are principally associated with precipitation and dissolution processes that yield calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H) (Taylor 1997, Hewlett 2004, Neville 1996, Neville and Brooks 2010). The degree of the relative proportions of hydraulic reaction to carbonation requirements (shown in Table 2.5) is important for understanding initial set and long term performance.

Table 2.5: Approximate hydraulic set vs. carbonation set (Forster 2004b)

Binder Type	Degree of Hydraulic Set	Degree of Carbonation	Compressive Strength
Non-hydraulic lime	0	100%	2 - 3 N/mm^2
NHL 2 (feebly hydraulic lime)	45% - 50%	50% - 55%	2 - 7 N/mm^2
NHL 3.5 (moderately hydraulic lime)	75% - 80%	20% - 25%	3.5 - 10 N/mm^2
NHL 5 (eminently hydraulic lime)	80% - 85%	15% - 20%	5 - 15 N/mm^2

Those hydraulic limes with high hydraulicity and low carbonation requirements are deemed to have a primary hydraulic set and a carbonation ‘side’ reaction (Hughes et al. 2007). This terminology reverses in low hydraulicity limes.

2.7 Lime Mortar Mix

Mortar is a mix of lime, an aggregate (such as sand) and water. Allen et al. (2003) argued that optimum and consistent performance of mortar requires correct constituent proportions. A typical modern lime mortar mix would be 1 part lime to 3 parts washed, well graded, sharp sand based on the theory that the voids of empty space between the sand particles account for a 1/3 of the volume of the sand (Allen et al. 2003).

2.7.1 Water

Water plays an integral role in the manufacture of mortars. It is essential for the hydration reaction to occur in the material but is fundamentally required to achieve suitable workability characteristics. Water that is included to a designed mix that goes beyond that required for full hydration will result in the development of the pore structure. Water therefore has a significant influence on the development of the physical properties of the material i.e. compressive strength, permeability etc. The function of water in the hydraulic reaction is to enable dissolution and precipitation reactions to occur. This yields relatively insoluble calcium silicate hydrates compounds that are both amorphous and crystalline. These are stable and have significantly lower solubility.

The quality of water can affect the setting and strength of mortar as stated in BS EN 1008: 2002 (Allen 2003). The water must be clean and free from suspended solids and dissolved salts. In general, water fit for drinking such as tap water is acceptable for mixing mortar. Excessive impurities in mixing water not only affect the setting time and mortar strength, but may cause efflorescence, staining, corrosion of reinforcement, volume instability, and reduced durability.

2.7.2 Aggregates

Aggregates are defined as granular materials used in construction that may be natural, manufactured or recycled (British Standards 2002). Aggregates are much cheaper than binder therefore using as much aggregate as possible in mortar (Jackson and Dhir 1996) will ultimately be more cost effective. Aggregates must be chosen carefully as they can comprise 50 to 75% of the total volume of mortar. Their type, size and physical properties will affect the material and construction process (Allen et al. 2003).

Generally, natural sands and gravels are used in mortars but other materials such as crushed shell, crushed rocks, sandstone are also frequently adopted for specific purposes (Gibbons and Newsom 2003). Aggregates can considerably improve the stability and durability of the resulting mortar, and must ideally be free from silt and clay to eliminate the possibility of failure (Allen et al. 2003).

2.7.2.1 Basic Characteristics of Aggregates

A good aggregate should produce designed properties in both fresh and hardened mortars. Evaluation of the properties of an aggregate are important and an understanding of its strength, and its effect upon the materials relative volumetric stability, porosity, relative density and chemical reactivity are essential.

An aggregate shape and surface texture can affect the properties of mortar in both plastic and hardened states. These external characteristics may be assessed by observation of the aggregate particles and classification of their particle shape and texture in accordance to BS EN 933-3: 1997. The classification is somewhat subjective due to visual analysis and identification of mineral components. However, the particle shape may also be assessed by direct measurement of the aggregate particles to determine the flakiness, elongation and angularity.

2.7.2.2 Aggregates Mechanical Behaviour

Several attributes of the aggregates have a significant influence on the mechanical behaviour of the mortar. This includes the determination of the grain-boundaries influence upon strength as stated by Hall–Petch equation (see Equation 2.2).

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

(Equation 2.2)

Where σ_y is the yield stress, σ_o is a materials constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion), k_y is the strengthening coefficient (a constant unique to each material), and d is the average grain diameter.

This is a method of determining the strength of materials by changing their average crystallite (grain) size. Hsiao and Zhang (2000) observed that grain boundaries impede dislocation movement and that the number of dislocations within a grain have an effect on how easily dislocations can traverse grain boundaries and travel from grain to grain. By changing grain size one can influence dislocation movement and yield strength.

Scottish lime mortars have been traditionally manufactured adopting silicate sands as a function of geological complexity and ease of mineral extraction. The effective bonding between lime and aggregate is clearly important. Lewin (1981) indicates that lime has a low affinity for siliceous substances. Conversely, lime based aggregates can have a positive strength relationship in these materials. Intuitively, rougher surfaces result in better mechanical bond strength. Additionally, the porosity of an aggregate plays a significant role interface strength development (Neville 1996). Lanas et al. (2006) suggests that the nature of the aggregate is a pivotal factor in increasing the mortar strength. This is especially pronounced in calcitic binders and fillers due to nucleating sites for the crystal growth of portlandite, and the transformation into calcite due to carbonation.

2.7.2.3 Aggregates Size

For the maximum effect of a calcitic filler to be noted it must be very fine and thoroughly mixed into the mortar. The fineness increases the surface area of calcium carbonate and enables it to readily interact with the binder (Hawkins et al. 2003). Pera et al. (1999) used 20μm (micron) finely ground marble as source of calcium carbonate inert filler. Clearly, the aggregates size must be given great considered and their relative surface area. Whilst positive effects have been reported in the introduction of fine calcitic material this can create problems with water ratios and workability (Farrar and Hawe 1985).

2.7.2.4 The Grading of an Aggregate

The grading of an aggregate defines the proportions of particles in different sizes. The size of the aggregates particles normally used in construction varies from 37.5mm to 0.15mm. BS EN 12620: 2002 places aggregates in three main categories; fine aggregates or sand (smaller than 5.00mm), coarse aggregate (larger than 5.00mm and combined aggregate (comprising both fine and coarse aggregates). The grading of an aggregate can have a considerable effect on workability and stability of mortar mix. A sieve analysis is used for determining the grading of an aggregate (British Standards 2002).

2.7.3 Curing

Hydraulic lime cures (harden) by hydration in which the chemical bonding in between binder and water take place (Ward-Harvey 2009). It is important to provide adequate moisture (water) until its required strength is achieved (Allen and Iano 2009). Curing can take place over long period of time; more than 365 days depending on the water/lime ratio, climate exposure (including temperature, humidity and pressure), carbonation rate, time and mortar thickness (Taylor 2002). Hanley and Pavia (2008) however suggested that 56 days is sufficient enough to study lime mortar early strength.

Unfavourable curing condition will create a number of problems that will affect the quality of mortar. In hot weather, rapid evaporation could expel the water needed for hydration process, causing premature shrinkage on mortar. The quantity of mixing water should be increased to accommodate the high rate of evaporation. Conversely, curing in cold weather will increased the possibility of frost attack as the water in the mortar will expand (about 9%) to form ice (Allen et al. 2003, French 2007). No chemical reaction (hydration) will occur because ice has no capability to hydrate the lime binder. It was suggested by Arnold (2003) that curing protection is important to maximize the hydration process thus maximizing the mortar strength and characteristics. It can be achieved by protecting the structure maintaining the required moisture levels and temperature during and in the infancy of the placement of the fresh materials (Taylor 2002, Allen et al. 2003, Allen and Iano 2009, Holmes and Wingate 2002, Forster et al. 2013, Forster 2004a, Forster 2004b, Forster 2004c).

2.8 Pore Structure Development

Hydration can be considered as a series of dissolution and precipitation reactions forming calcium silicates hydrates (C-S-H) and calcium aluminates hydrates (C-A-H) (Forster 2004b). As the precipitated hydrates develop, the workability of the binder starts to reduce (the mortar starts to harden). The products of hydration developed, as the moisture evaporates, and the pore structure of the mortar is formed by fill up the space where the water once resided (Hughes and Valek 2003).

2.8.1 Properties of Pore Structure

Voids between the hydrates form the pore structure. The pore structure is a very important micro-structural characteristic in a porous solid because it influences the physical and mechanical properties and greatly influences the durability of the material. These effects can be seen in Table 2.6 (Aligizaki 2006).

Table 2.6: Properties affected by pore structure (Aligizaki 2006)

Properties	Influence
Compressive strength	Primarily affected by the total volume of the pores, size and the spatial distribution of pores, maximum pore sizes, pore shapes and connectivity.
Elasticity	
Permeability and diffusivity	Influenced by the total volume, size, shape and connectivity of the pores
Shrinkage	Largely a function of changes in surface energy at the pore walls
Freezing and thawing	Controlled by the volume and the spacing of entrained air voids

The pore structure has a direct influence on permeability and related moisture transport processes in the mortar (Teutonico et al. 1999). The greater the hydraulicity in a mortar, the less permeable it is. The increasing densification of the products of hydration caused the permeability to decrease (Hughes and Valek 2003, Banfill and Forster 1999, Forster 2004b). Digital Image Analysis (DIA) and Scanning Electron Microscopy (SEM) methods have been shown to differentiate differences in pore sizes and distribution in lime mortars as shown in Figure 2.9 (Lawrence et al. 2007).

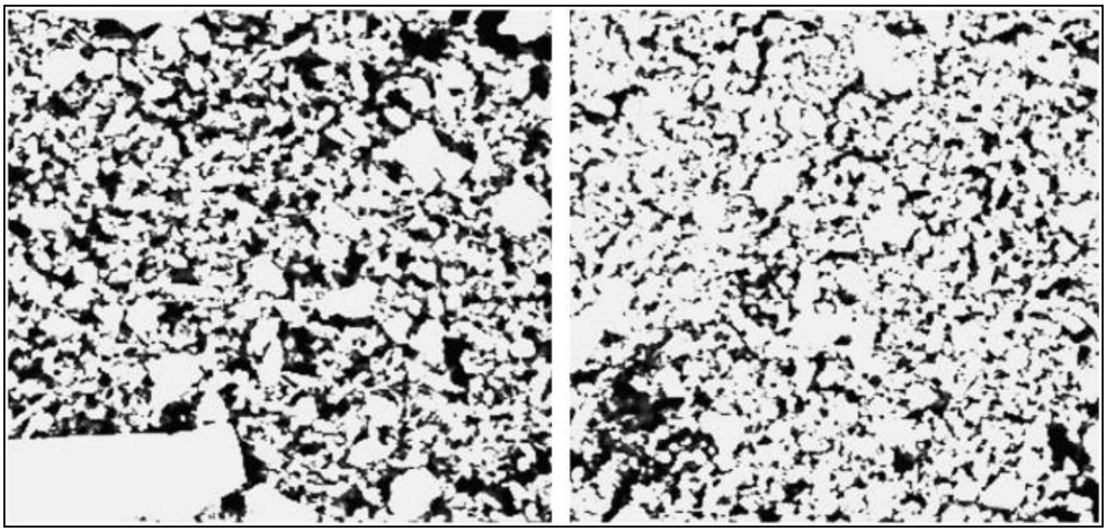


Figure 2.9: Digital Image Analysis (DIA) image of a back-scatter mode SEM micrograph of uncarbonated (left) and carbonated (right) pore structure of an oolitic lime mortar (width of each image 20 µm). Dark pixel indicate pore and higher porosity area (Lawrence et al. 2007)

The influence of the pore structure on durability of a material is significant. For porous materials, the moisture content at the time of freezing is a critical factor (Said 2006). The risk of frost damage also depends on the rate of freezing and on the pore structure of the material. Freezing is a gradual process, occurring from the surface advancing inwards. As ice crystals form in the outer pores they, result in an increase in volume water expands by about 9% of its volume when it freezes (French 2007) and in turn results in water being pressurised and expelled into adjacent connected pores. The result is a progressive build-up in hydraulic pressure if those pores that are also full of water (Illston et al. 2001).

2.8.2 Breathability (Vapour Permeability)

Natural hydraulic lime mortars are relatively flexible, allowing for movement in the building and thus preventing cracks in the masonry. Hydraulicity and therefore the strength of lime have been shown to have a relationship with water vapour permeability. Conversely, vapour permeability of mortar improves with increasing free lime content. Low hydraulicity lime mortar has been shown to allow water vapour to readily diffuse from the building enabling the structure to effectively 'breathe' (Holmes and Wingate 2002, Banfill and Forster 1999, Forster 2002).

Vapour permeability is an important physical characteristic as it enables any moisture to escape from the walls. This can aid in the control of condensation and damp within the building (most modern renders, plasters, mortars and paints are impervious, trapping moisture leading to problems such as condensation, mould growth and even degradation of the fabric of the building such as timbers rotting, bricks/masonry crumbling). This characteristic also provides a degree of thermal insulation due to modified conductivity of the material (Bridgwood and Lennie 2013).

2.8.3 Sorptivity

Permeability is one measure of a mortar's ability to transport water. It influences the transport of both gas and liquid phases. In 1957, John Philip introduced the term 'sorptivity' and characterized it as a "*measure of the capacity of the medium to absorb or de-sorb liquid by capillarity*" (Dane and Topp 2002, Appels 2013). Sorptivity is widely used in characterizing soils and porous construction materials such as brick, stone and concrete.

Hall & Hoff (2012), modified the definition of sorptivity as "mortar ability to absorb and transmit water through it by capillary suction" (Hall and Hoff 2012). Sorptivity determines information relating to the entire pore structure and provide gross transport properties of the mortar. It is recognised that limitations exist with sorptivity testing in so much as it does not yield direct information on the pore size or pore size distribution. The initial rate of sorptivity is always greater than subsequent measurements, due to the larger pores are being filled first, regardless the mixture or formulation (Kerr 2008).

Sorptivity is practically very important in the evaluation of rising damp. Rising damp is a well known phenomenon around the world and occurs when groundwater flows into the base of a construction and is allowed to rise through the pore structure (Rirsch and Zhang 2010). The dampness can cause damage to the materials fabric and adversely influence internal comfort conditions.

Sorptivity is influenced by sampling location and it has been shown that sorptivity values determined on concrete taken from the top surface of a concrete cube can be several times greater than those for concrete taken from the bottom surface of the cube (Khatib and Mangat 1995). Carbonation influences sorptivity (Dias 2000). Table 2.7 shows the water absorption properties of some mortars (Rirsch et al. 2011).

Table 2.7: Water absorbing properties of some mortars (Rirsch et al. 2011)

Sample	Sorptivity ($mm/min^{0.5}$)	pH	Water absorption (wt.% at 24 hours)
6 months old - modern mortar	0.3	12.1	9.0
110 years old – brick wall terraced house	1.3	9.2	19.1
160 years old – lime mortar stone wall	4.6	9.0	22.8
15 years old – pointing	0.2	11.9	2.5
160 years – solid stone wall	14.0	8.5	25.0
140 years old – brick wall	4.1	9.0	19.2
400 years old – stone wall	0.5	8.7	10.0

Compressive strength of specimens increases with decrease in sorptivity and vice versa (Tokchom et al. 2009). It is due to porosity because mortar itself is a porous composite material consisting of mineral aggregates and the binder matrix that form a durable structure (Gonen and Yazicioglu 2007). The porosity of the mortar allows movement and retention of water and gas (particularly CO_2) (Steffens et al. 2002).

In the case of additive and admixture, the fineness of filler is important for the modification of aggregates-mortar interface zone in which is the weakest link in the mortar (Tasdemir 2003). This small particle size filler can fill in the voids of the binder matrix and cause the pore structure to become denser. This in turn increases the compressive strength but lowers the sorptivity value.

O'Farrell et al. (2001) believed that the presence of admixture does not affect on the water absorption of mortar but sorptivity however, is affected significantly by not only the presence of admixture but also by composition. Sorptivity also varied with material composition and substitution. In his research on sorptivity and strength of air cured and water cured Portland cement–pulverised fuel ash–metakaolin (PC-PFA-MK) concrete, Bai et al. (2002) found that the increasing the metakaolin (MK) content of water cured PC–PFA–MK concrete reduces the sorptivity to values below that of the control. This is opposed to the sorptivity of PC–PFA concrete which exceeds the control. In another study by Hadj-sadok et al. (2011), the sorptivity of mortar was improved by the presence of ground granulated blast furnace slag (GGBFS), especially for 50% substitution rate. However, a little evolution of capillary absorption is observed between 90 and 360 days. Olivia and Nikraz (2011) suggested that the sorptivity values can be improved by a decreasing the water content and increasing the binder content but Deb et al. (2013) argued that the results depends on the type of mortar.

2.9 Mechanical Properties of Lime Mortar

Wet mortars have excellent properties that allow the bricklayer to use less effort to place the mortar and produce masonry that has fully filled joints. This can improve building performance, especially obviating moisture ingress and air-tightness. The hardened mortar can be designed to exhibit the appropriate physical characteristics required to have a high degree of compatibility with the masonry units to provide more durable buildings. Any hardened mortar requires the satisfaction of certain specific key requirements including; compressive strength, flexural resistance and low elastic modulus, vapour permeability, long term bond strength and autogenous healing of fine cracks.

The strength of mortar is defined as the maximum load (stress) it can carry. As the strength of mortar increases, a corresponding improvement in other properties is also noted. The prevalence of compressive strength testing therefore reflects this situation (Jackson and Dhir 1996). Mortars and concretes are comparatively brittle materials that are relatively weak in tension.

Mortar mixes and classes can be selected to provide a wide range of mechanical and durability properties to meet design requirements. The conformation of mixture can be achieved by conducting test on the mortar properties. Test methods for all building limes are covered in EN 459-1:2010. This document describes the reference methods and, in certain cases, an alternative method which can be considered to be equivalent.

2.9.1 Flexural Strength

The stress-strain behaviour of brittle materials is not usually ascertained by tensile testing. This is due to three significant reasons; (i) it is difficult to prepare; (ii) it is difficult to grip brittle materials without fracturing then and (iii) brittle material fail after only 0.1% strain (Callister 2010). Therefore, a more suitable transverse bending test is employed known as flexural strength as shown in Figure 2.10.

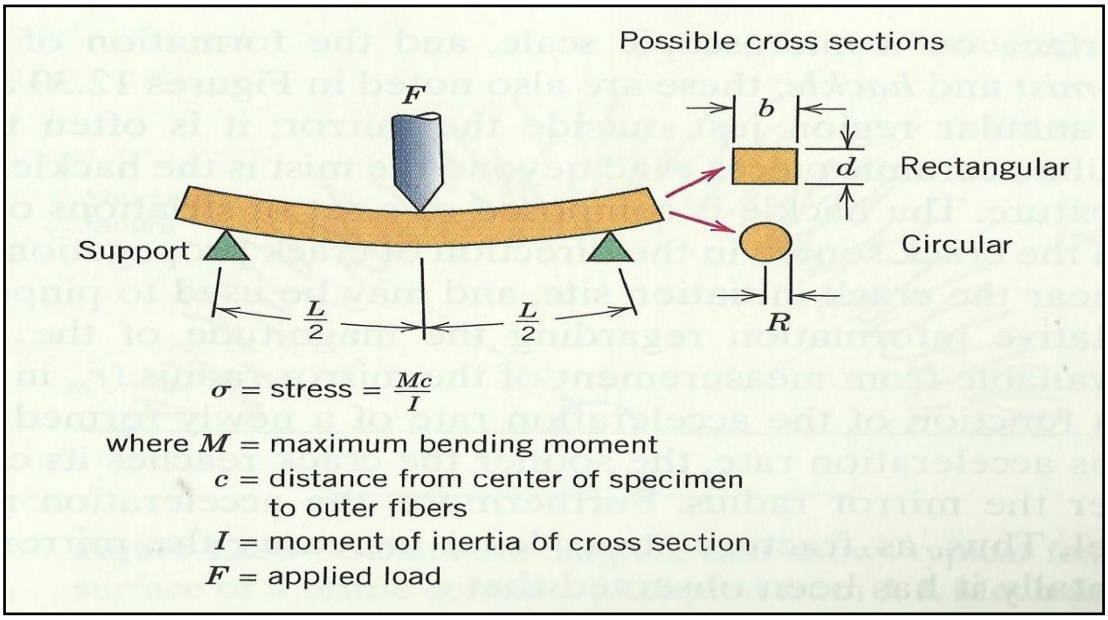


Figure 2.10: Flexural Strength Test Schematic Diagram (Callister 2010)

Flexural strength is usually calculated for concrete beam and slab (Almusallam et al. 1996, Teng et al. 2003, Tavakkolizadeh and Saadatmanesh 2003). It is important to identify the mortar's ability to bend before it experiences major deformation (Rashid and Mansur 2005, Sivakumar and Santhanam 2007). A mortar's flexural strength also correlates with its tensile strength, or the mortar's ability to be stretched without significantly changing its shape (Almusallam et al. 1996).

Mortar is strong in compressive strength but is weak in flexural strength due to its brittle characteristic that limit the mortar usage in modern construction (Pavia and Hanley 2009, Cobb 2009). A reduction in flexural strength as percentage of the compressive strength indicates reduced plasticity and increased brittleness as shown in Table 2.8 (Allen et al. 2003).

Table 2.8: Relationship between flexural and compressive strengths of NHL 3.5 mortar (Allen et al. 2003)

Age (days)	Flexural strength (as % of compressive strength (1:3 mix proportion by volume)
7	80
14	70
28	67
56	65

Flexural strength of a mortar can be increased by modifying the mortar mix. Usually the lime filler or powder was added as a binder. According to Lanas et al. (2006a), mortar with more binder content would achieved a higher flexural strength. This finding was in agreement with research by Moropoulou et al. (2005) who was successfully proved that adding a filler that is similar to binder can produce higher flexural strength as the filler has the same reaction as the parent material in binder. Time and binder/aggregates ratio are also important factors in increasing flexural strength as concluded by Lanas and Alvarez-Galindo (2006) who found that flexural strength at 365 days was doubled compared to 28 days (see Figure 2.11).

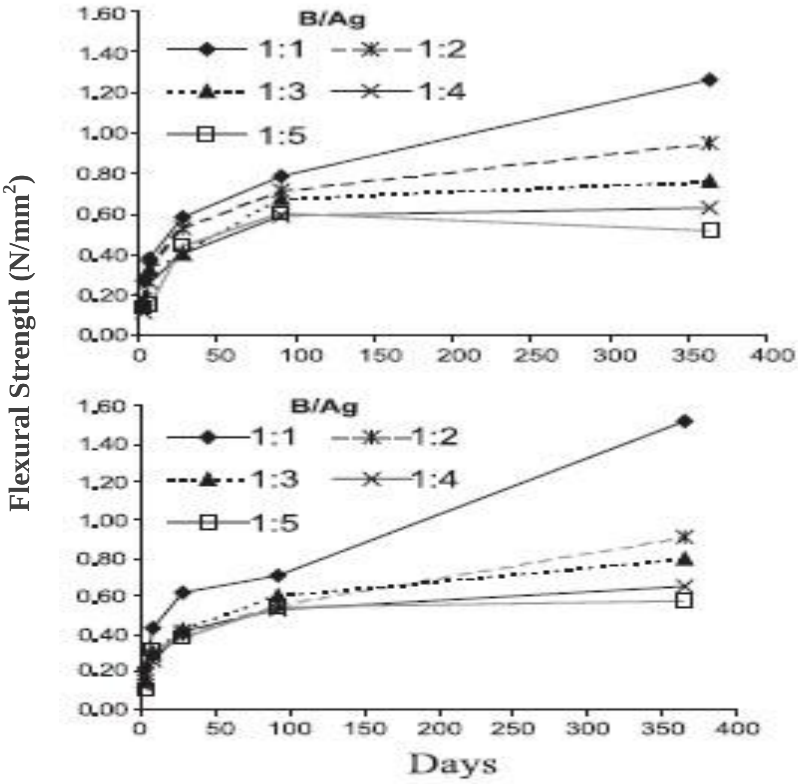


Figure 2.11: Flexural strength of lime mortar with two different calcitic aggregates (Lanas and Alvarez-Galindo 2006)

2.9.2 *Compressive Strength*

Compressive strength is an expression of how much uniaxial compressive stress the material tolerates before collapsing (Berge 2000). Compressive strength of the mortar is most common performance measure used by architect, engineer and specifier in construction projects. The compressive strength is calculated from the failure load divided by the cross-sectional area resisting the load (Callister 2010).

The compressive strength of mortar is sometimes used as a principal criterion for selecting mortar type (Neville 2002, Neville and Brooks 2010, Forster 2004b). Its prevalence has occurred due to it being relatively easy to measure, and it commonly relates to some other properties, such as tensile strength, flexural strength and absorption of the mortar (Malhotra 2006, Garber 2006).

The compressive strength of mortar depends largely upon the lime content and the water-binder (lime) ratio. There is a large volume of published studies describing this method researcher in determining the mechanical behaviours of concrete and mortar (Bushlaibi and Alshamsi 2002, Guemmadi et al. 2009, Benachour et al. 2008, Benachour et al. 2009, Lanas and Alvarez-Galindo 2006, Lanas et al. 2006b, Yang et al. 2010, Li et al. 2009, Lian and Zunge 2010, Aruntaş et al. 2010, Binici et al. 2008, Ezziane et al. 2007, Tanyildizi and Coskun 2008, Uysala and Tanyildizi 2012). Lanas and Alvarez-Galindo (2006) also enlisted time and binder/aggregates ratio are also important factors in increasing compressive strength (see Figure 2.12).

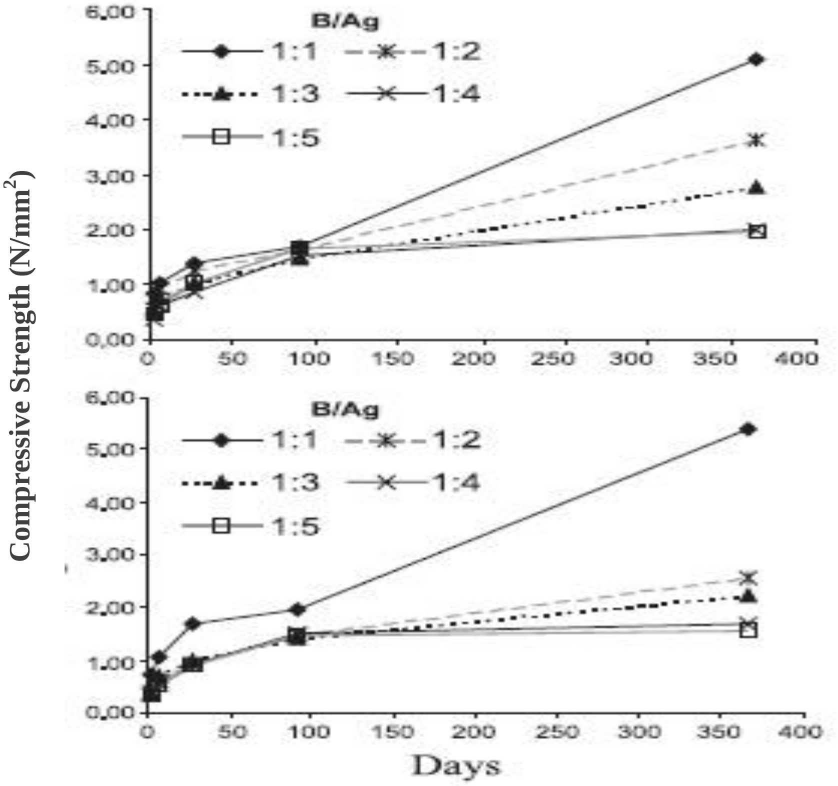


Figure 2.12: Compressive strength of lime mortar with two different calcitic aggregates (Lanas and Alvarez-Galindo 2006)

2.10 Micro-structural Characteristics

Several techniques have been developed to characterize the pore structure of mortar. This is important to satisfy the need to understand the resulting hydration products of the mortar and binder aggregate interface. Additionally, the importance of evaluating the size, connectivity and distribution of the pore structure via Scanning Electron Microscopy (SEM) is also helpful. Elsen (2006) suggested the usage of optical microscopy in studying historic mortars and for the study of the interfacial zone, the bonding and possible reaction rims between aggregates, bricks or stone and the mortar.

For the durability of mortar, permeability is believed to be the most important characteristic, which is related to its micro-structural properties, such as the size, distribution, and interconnection of pores and micro-cracks (Savas 2000). The micro-structural investigations shed some light on the nature of interfacial bond of fibres and the mortar paste and its effect on its mechanical and fracture properties (El-Dieb 2009). Lee at al. (2003) applied micro-structural analysis to confirm their findings on ettringite formation at early curing stages of fly ash–cement pastes containing activators.

SEM was used to characterise the morphology and analytical composition of the ancient covering plaster mortars from several convents and Islamic and Gothic palaces in Palma de Mallorca (Genestar and Pons 2003). Hughes and Cuthbert (2000) utilized both microstructure and petrography analysis in their studies on medieval lime mortars from the west of Scotland.

2.10.1 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition (Egerton 2005). SEM provides the investigator with a highly magnified image of a micro-structural changes than can be achieved by using optical microscopy (OM) (Lawrence 2006).

There is a large volume of published studies describing the role of SEM in investigations of lime mortar micro-structural changes (Gleize et al. 2003, Sepulcre-Aguilar and Hernández-Olivares 2010, Yang et al. 2011). SEM micrographs, can identify some of the significant C–S–H rod network can be seen throughout the specimen analysed. SEM microphotograph of natural hydraulic mortars can also identify C–S–H rod networks. The identification of C-S-H and the interface between silica aggregate and mortar matrix is shown in Figure 2.13.

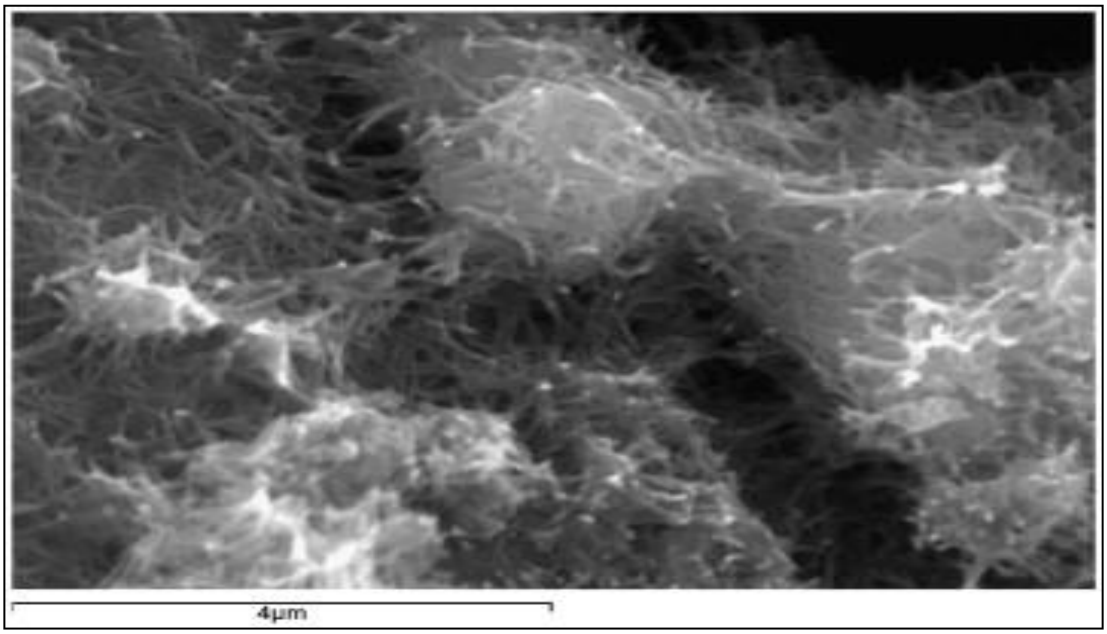


Figure 2.13: SEM image of NHL (Sepulcre-Aguilar and Hernández-Olivares 2010)

By using SEM, not only topographical information can be produced, but information concerning the composition near surface regions of the materials is provided as well (Bindell 1992). SEM is used to understand the complex nature of mortars having the major advantage that the pore structure has an image and the exact position of the pore can be located (Stefanidou 2010). In this way pores and cracks occurring inside the matrix or in the transition zone can be distinguished. Additionally, a wide range of pore sizes can be measured.

Microscopic examination shows a particular area of the sample under a particular set of preparation and observation conditions (Lindqvist and Sandstrom 2000). SEM was furthermore being utilized in order to observe differences of structure and texture between different mortar formulations (Ventolà et al. 2013) as shown in Figure 2.14. Through SEM analysis, Izaguirre et al. (2009) (see Figure 2.15) found an air void caused by insolubility of anionic surfactants that were used as additives.

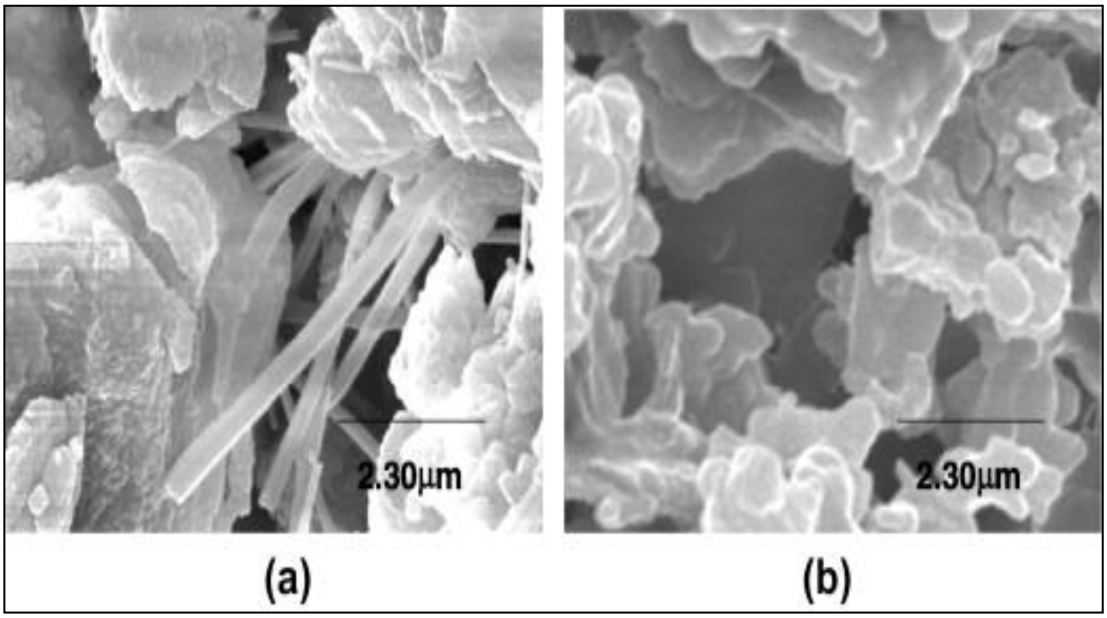


Figure 2.14: SEM images of lime mortar specimens between (a) modified mortar - acicular crystals of aragonite ($CaCO_3$) can be identified and (b) control mortar (Ventolà et al. 2013)

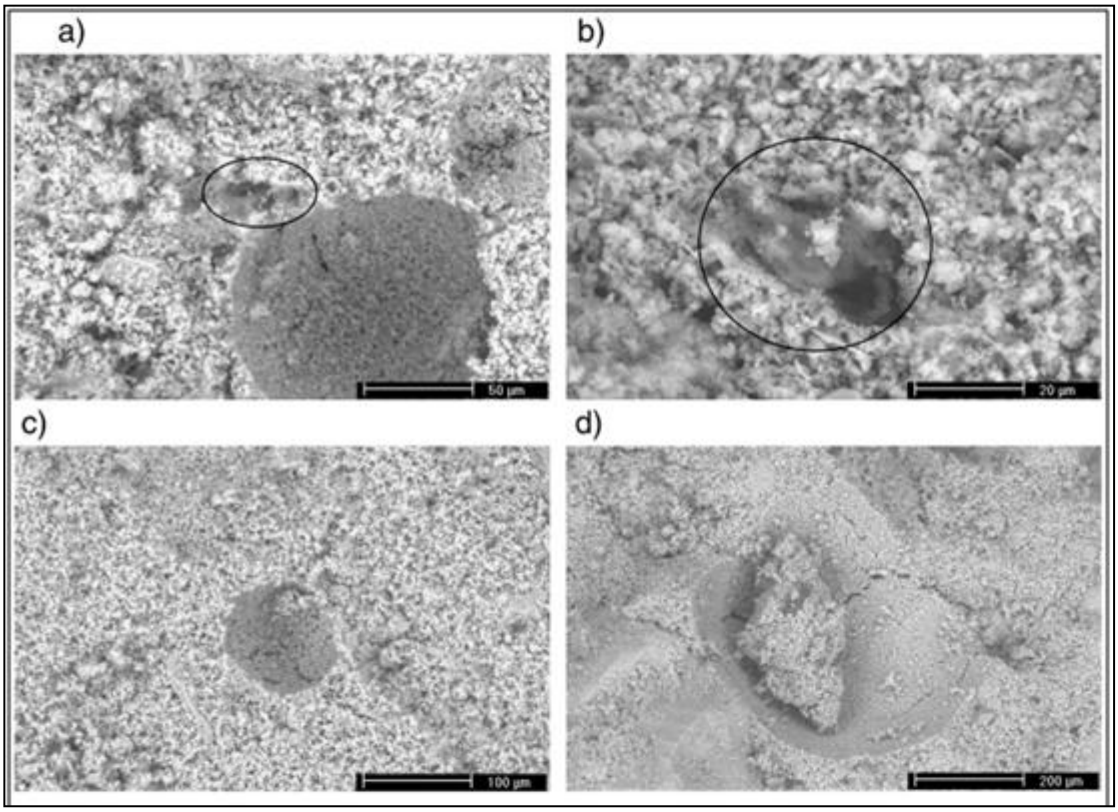


Figure 2.15: SEM images obtained for different mortars. Images (a) – (d) shows a air voids due the insolubility of additives used (Izaguirre et al. 2009)

2.10.2 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a technique used to identify the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of X-rays to diffract into many specific directions (Schwarzer 2005). In mortar mineralogy analysis, XRD is used to establish the crystalline structure and to measure the composition present in specimens (Toney 1992, Kalagri et al. 2014). Katayoon (2007) described the mechanism of XRD;

> *"When a monochromatic X-radiation strikes adjacent atomic planes of a crystal, the scattered rays interfere with each other as they leave the crystal. The wavelength is approximately equal to the inter-atomic spacing. When Bragg-Brentano geometry is met, the X-rays scattered from the crystalline planes interfere constructively, producing a diffracted beam. The conditions satisfying this are defined by Bragg's equation (Equation 2.3)"*

$$n\lambda = 2d.\sin\theta$$

(Equation 2.3)

In which n is the diffraction order, λ is the wavelength of the incident X-ray beam, θ is half the diffraction angle (the scattering angle at which an intensity peak is detected), and d is the inter-plane spacing. Figure 2.16 illustrates the diffraction phenomenon in relation to Bragg`s equation.

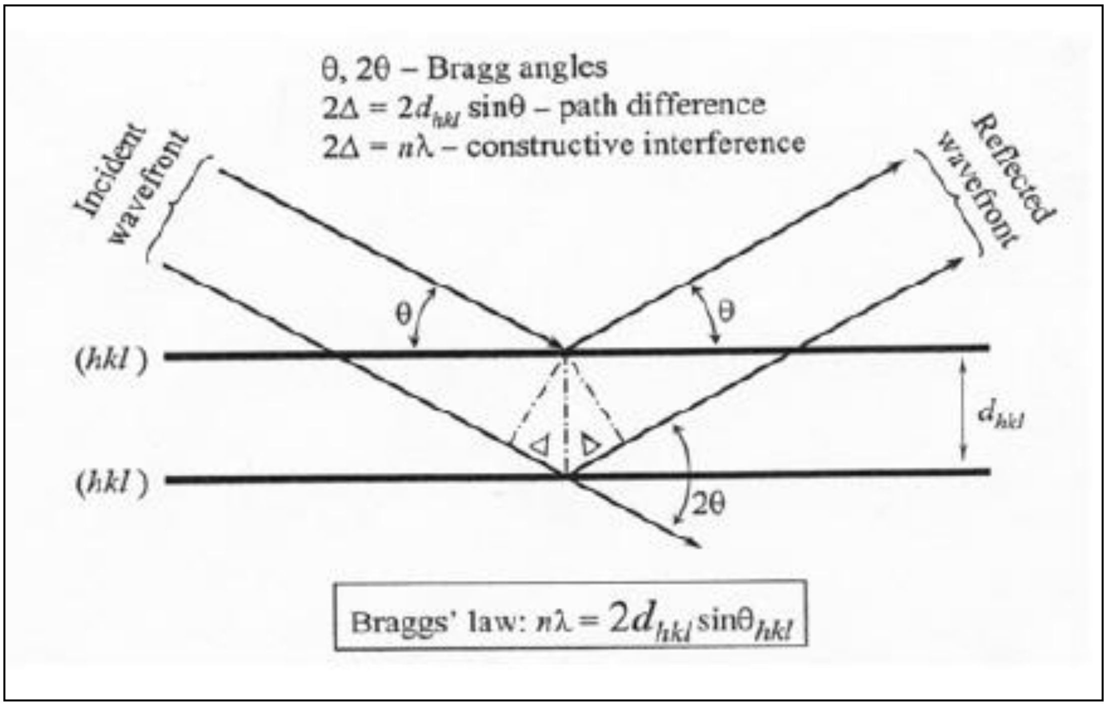


Figure 2.16: Diffraction phenomenon concerning Bragg`s equation (Guinier 1994)

XRD allows rapid detection of crystalline components of lime binder and mortar (Kalagri et al. 2014, Middendorf et al. 2005). Usual instrumentations and techniques do not allow detection of component present in amount less than a few percent (Malhotra

2006). The technique is widely used in lime mortar investigations particularly to identify specific material in historic mortars (Lanas et al. 2005, Marques et al. 2006, Moropoulou et al. 1995, Moropoulou et al. 2000). In his study on amelioration of the properties of hydrated lime, Skoulikidis (1996) identified traces of aragonite from mortar carbonation process by using XRD analysis.

2.10.3 Petrographic Analysis

Petrographic analysis is a technique originally developed for earth science study to observe rocks and minerals (Derr 2012, Sheherbakov and Belousov 2002). It is done by creating a "thin-section" of the material of exactly 0.03 mm thick (Rapp 2009). The thin section of the material is viewed using polarised microscope fitted with two polarizing filters oriented at right angles to each other (Civan 2000). This filters are use to block any light during observation. Ellis (2006) found that some samples containing minerals may diffract the light; making it visible in cross polarized light. It is proven that petrography analysis in combination with chemical analysis can allow estimation of the original mortar proportions and the possible cause(s) of mortar behaviour (Stutzman 1994, Pavia and Caro 2008, Hughes and Cuthbert 2000).

Petrographic analysis is widely used in fire investigation of masonry structures built of materials such as stone, brick and mortar (Riley 1991, Georgali and Tsakiridis 2005). It is done by an assessment of micro-cracking and mineralogical changes due to the depth of fire and vital for accurate detection of damaged, which provides economical benefit during building repair and improved safety assurance (Ingram 2009). Figure 2.17 and 2.18 show examples of petrography images of mortars.

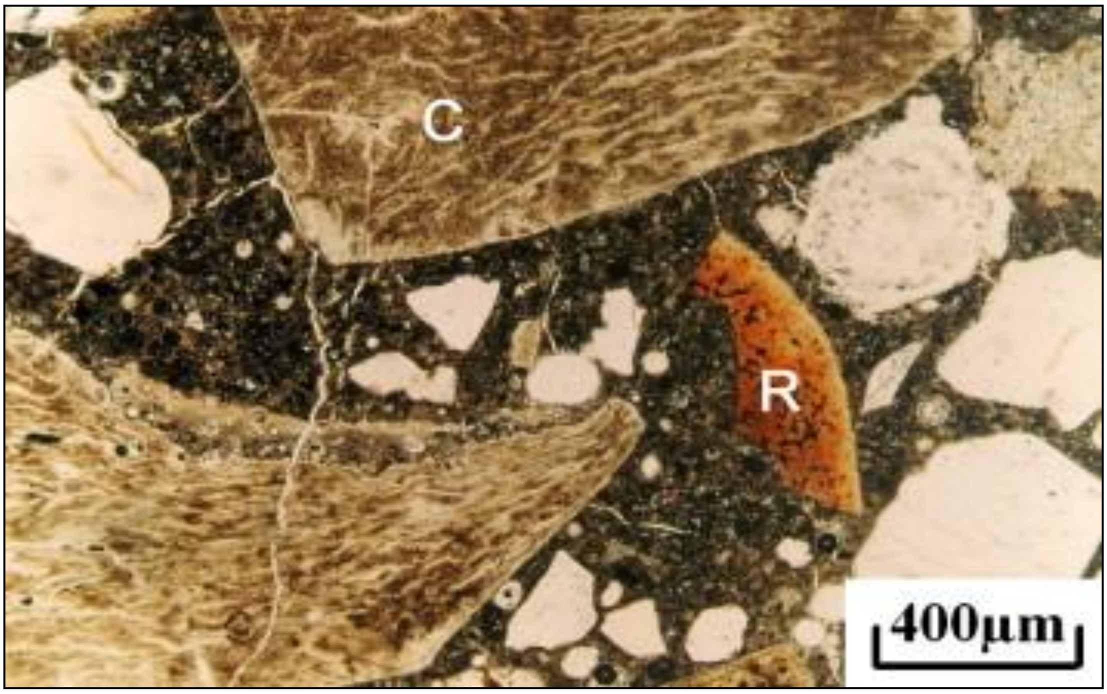


Figure 2.17: Petrographic image. A photo micrograph of concrete in plane polarised light. The image is showing both reddened (red, marked R) and calcined (brown mottled, marked C) flint aggregate particles. Numerous fine cracks (white) within the cement matrix (dark), some of which radiate from quartz fine aggregate (white) (Ingram 2009)

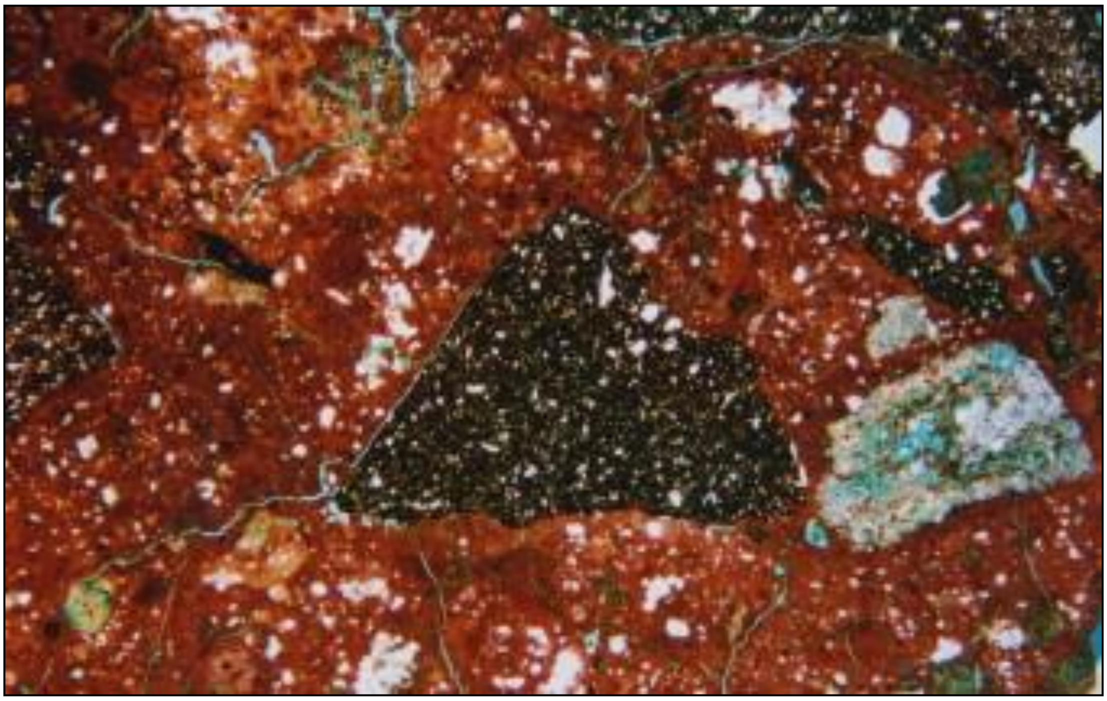


Figure 2.18: Petrography of lime mortar. Image shows angular ceramic aggregate in a fine-grained, homogeneous, cohesive binder of carbonated lime which remains unaltered (Pavia and Caro 2008)

2.11 Environmental Issues with Lime and Cement Production

Lime manufacturing causes adverse environmental impacts at every stage of its production. In quarrying, crushing, screening and conveying of limestone can produce a massive amount of dust (Oates 1998). Quarrying also causes unwanted vibration due to machinery operation, aqueous discharges, disposal of solid waste and noise as a result of blasting. Importantly, detriment to the landscape is all to frequent and this is especially pronounced in rural settings (Oates 1998).

2.11.1 Issues on Carbon Footprint

The calcination of lime is a significant contributor to carbon dioxide emissions. The CO_2 liberated in the dissociation from the lime stone and that associated with the fuel required to achieve that relatively high kiln temperature both have environmental costs (Meier et al. 2006). Calcination processes produce carbon dioxide when calcium carbonate is heated, yeilding lime and carbon dioxide. Indirectly CO_2 is generated through the production of energy (Li 2004). Lime production has been estimated to produce approximately 800kg of CO_2per tonne, in which total energy usage are ranges from 3600 kJ/kg of calcium oxide for vertical double shaft kilns to 7500 kJ/kg of calcium oxide for non-preheated long rotary kilns (Oates 1998, Boynton 1980).

Clearly both the cement and lime industry are facing several challenges in reducing its carbon dioxide emissions (Wang et al. 2004). Emerging climate change policies have the potential to place the industry at significant financial risk. Current practice and pollution abatement is not sought (Mahasenan et al. 2003) in the truly meaningful capacity required to meet CO_2 reduction targets.

Mahasenan (2005) establishes three main problems faced by the industry; (i) the industry is heavily depending on high carbon fossil fuels; (ii) the technology used to produce limestone based clinker and, (iii) the sustainability of limestone and fuel stocks. The third problem is very important especially for regions where future demand is expected to be high (Mahasenan et al. 2003).

2.12 Sustainability in Built Environment

Ecological design in built environment was introduced to achieve environmental goal for sustainable life (Kibert 2008). It is accomplished by using an integrated approach of designs so that the negative impacts of building on the environment could be only marginal (Ali and Al Nsairat 2009). Sustainability has emerged as a new building philosophy, encouraging the use of environmental ethics, passive bioclimatic design, environmental responsible building material selection, life cycle assessment (LCA) and waste reduction (Graedel 1999, Castro-Lacouture et al. 2009, Kibert 1999). Utilization of low carbon materials represents an important approach in designing new building (Yudelson 2007).

2.12.1 Environmental Assessment Tool

There are a variety of tools for the environmental assessment of the built environment. The assessment mainly focuses on energy, indoor and outdoor climates, building materials and many other aspects (Forsberg and von Malmborg 2004). Malin (1999) identified nine key issues (see Figure 2.19) for choosing building materials based on life cycle assessment. Most of the issues relate to embodied energy used in manufacturing and transportation of building materials. Transportation contributes significantly to embodied energy, and clearly conflicts with sustainability strategies due to pollution associated with the fuels used (Trumbull 1999, Lowe 1999, Graham 2003). In addition, even regionally sourced products cannot guarantee a minimal carbon footprint in transportation (Malin 1999).

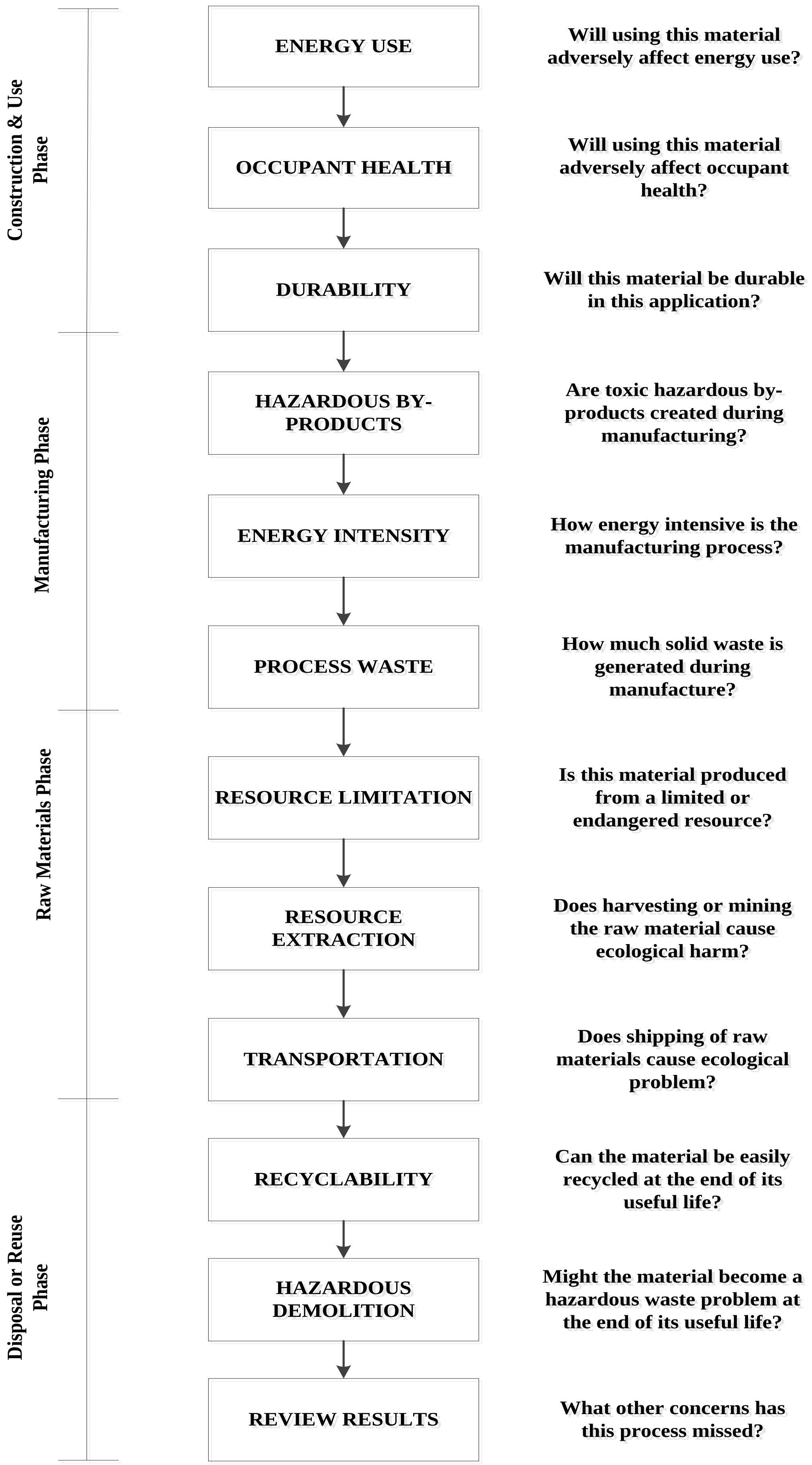


Figure 2.19: Nine key issues in choosing building materials (Malin 1999)

2.12.2 Current Practice

Within world-wide current construction practice, Ordinary Portland Cement (OPC) is the most commonly adopted binder. This is regardless of the climatic conditions (Hughes et al. 2003) the materials are ultimately exposed to. Ordinary Portland Cement is relatively economical, durable and achieves high compressive strength (50 MPa) within short time frames (typically gaining 80-90% of its strengths within 28 days) (Neville 1996). The most common use for Portland cement is in the production of concrete.

It has been estimated that 3.6 billion tonnes of concrete are globally used each year (Felice 2013). Figure 2.20 (IMF 2013) indicates the relative use of cement by country in 2012. Concrete is the most widely adopted construction material on Earth, and its use is continuing to grow. The rate of concrete uptake in built environment is 10km^3/year. The relative size of the market is high especially set within the context of the volume of other potential substitutes (i.e. 1.3km^3/year of timber and 0.1km^3/year of steel). The annual figures in construction and is expected to rise (Felice 2013).

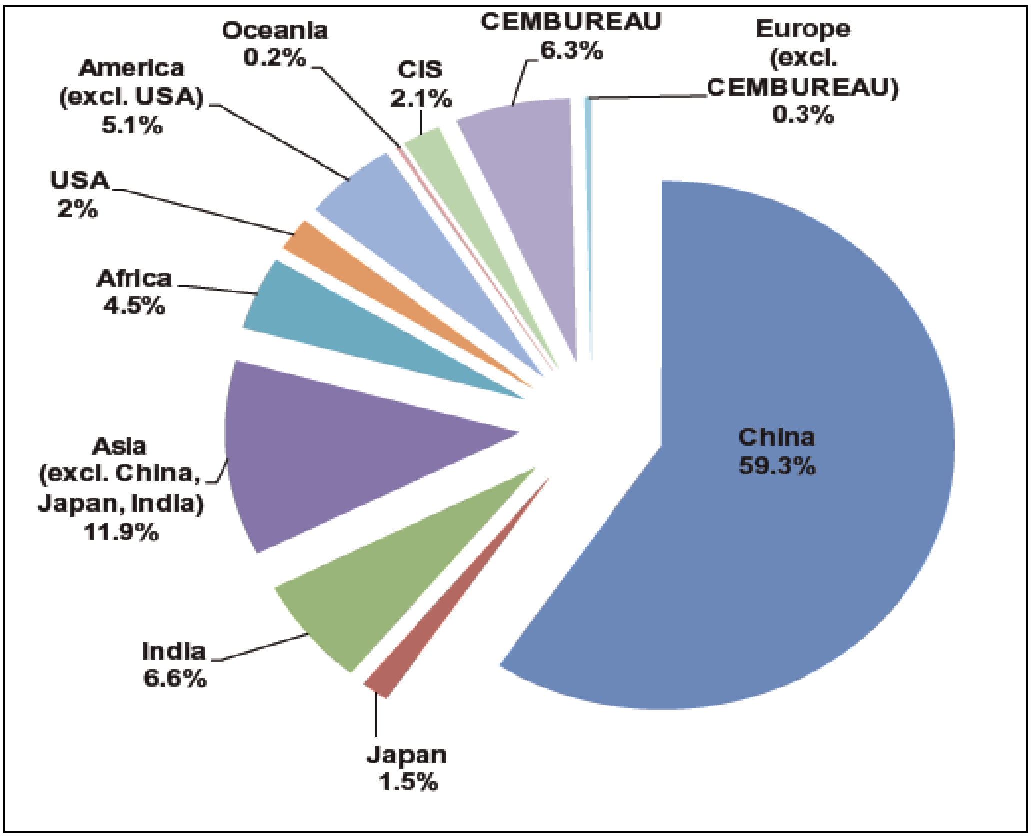


Figure 2.20: World Cement Production in 2012 (IMF 2013)

2.12.3 Concrete Production Impact on Environment

The quantity of concrete utilised in the world-wide market leads to significant environmental issues. The environmental performance has been criticised for decades as it has a high carbon footprint that contributes to approximately, 5% of annual anthropogenic global CO_2 production (Crow 2008). The sustained utilisation of concrete is due to its high durability, familiarity of use and a lack of viable substitute products (Felice 2013, Malin 1999). That said, as we move towards a carbon economy the uptake and drive for alternative binders will be more pronounced.

According to Barrientos and Soria (2010), global productions of hydraulic cement was estimated at 3310 million metric tons. On average one ton of CO_2 is emitted per ton of cement (Wilkinson 2009). The continued increasing uptake (see Figure 2.21) of cement use will result in corresponding CO_2 levels. This data cannot be accurately predicted due to disparities in the figures submitted by individual manufacturers that vary considerably according to process efficiency and their calculation method (Wilkinson 2009).

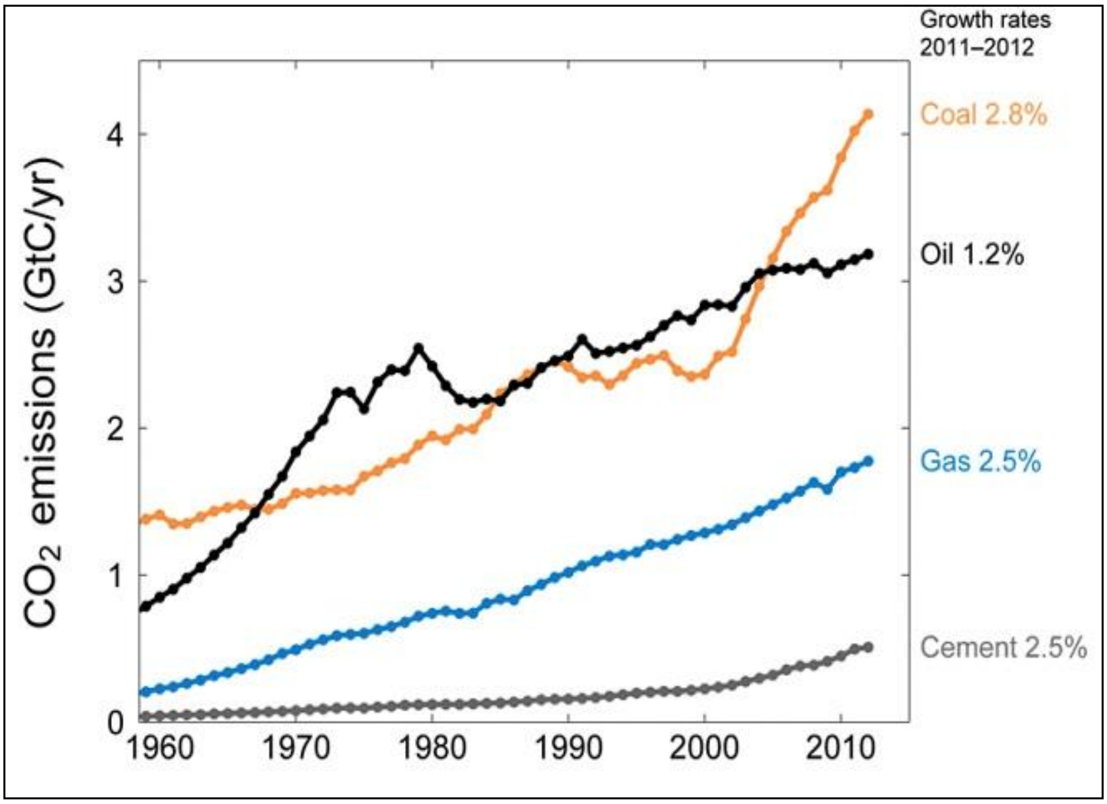


Figure 2.21: Global CO_2 emission (Le Quere 2013)

Concrete production is extremely carbon intensive as it releases CO_2 into the atmosphere (Graham 2003) from the limestone calcination (disassociation of CO_2 from $CaCO_3$ yielding CaO) (Virdi 2012), but also requires large energy input in the kiln firing process at 1500°C. Typically the manufacturing of Ordinary Portland Cement, the raw materials (typically limestone, clay or shale) are thoroughly mixed and heated, to a temperature of approximately 1450°C (Taylor 1997).

Hydraulic lime is considerably more environmentally friendly than Ordinary Portland Cement due to lime’s lower firing temperature (900°C) during the calcination process (Smith et al. 2005). The manufacture of limes both hydraulic and non-hydraulic consumes less energy and produces less greenhouse gases than Ordinary Portland Cement per unit weight (Mahasenan et al. 2003). This clearly creates favourable reference point for energy reduction via kiln fuel efficiency and broader reduction via processing. In addition, environmental benefits are associated with the carbonation process that occurs as part of the setting process of limes the sequestering of a proportion of the carbon dioxide emitted during the calcination process (Wilkinson 2009).

2.12.4 Adoption of Alternative Binders

It has been recognised that possibilities exist for the substitution of OPC with lime binders (Sickels-Taves and Sheehan 2002). Materials substitution must be seen within the context of expected performance and holistic design. Clearly, lime cannot be utilised for all modern construction processes but it has significant potential for uptake in many applications.

Variations in environmental conditions, such as relative humidity and temperature, influence the performance of lime and cement mortars alike. The widespread adoption of alternative binders plays an ever increasing role in carbon dioxide abatement and green construction.

Sickels-Taves and Allsopp (2005) figuratively illustrate the modern driving forces for the use of lime in the 21st Century (Figure 2.22). They suggested that lime is an effective catalyst for the 21st century’s competing priorities; and substantiate its use. Today, these issues are well established with ‘Sustainability,’ ‘Healthy Buildings,’ and

‘Heritage Conservation’ being initial motivating themes. These facets integrate into broader economic and political agendas of many developed countries.

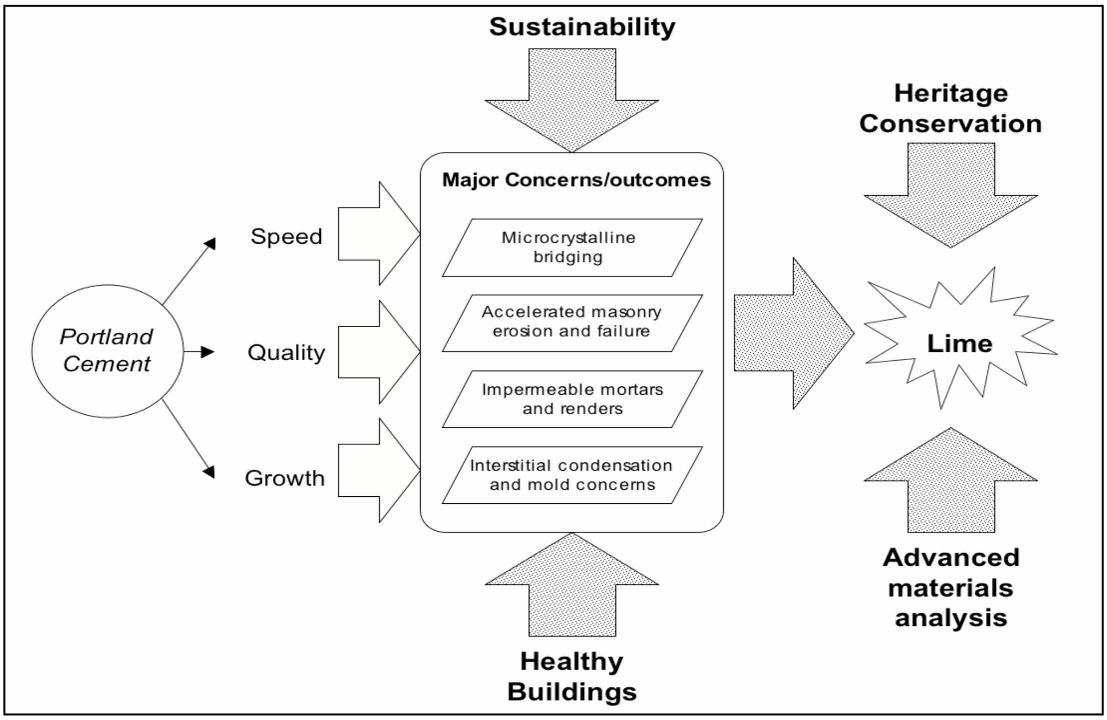


Figure 2.22: Lime 21st century imperatives (Sickels-Taves and Allsopp 2005).

Supporting the growing uptake in alternative binders are modern scientific methods. The relative size of research in the cement industry is considerable and understanding in materials characteristics and performance is well developed. The same cannot be said for lime science that has many unanswered parameters.

2.13 Performance and Environment of Natural Hydraulic Lime Mortar

Different parts of the world have different climates; some of which may be considered extreme within the context of lime works. Once buildings are complete, they gradually deteriorate according to the conditions of their use their environment that surrounds them (Tanabe 2008). Oliver (2005) suggested that material stress resulting from adverse climatic conditions is not as pronounced as a tangible consideration as it should be and this is reflected in an absence of standards in the industry. Ward-Harvey (2009) emphasizes that it is an important consideration due to the local climatic conditions that vary considerably and materials perform differently according to climatic exposure. The climate has a major effect in the functionality of a building and significantly affects the life span, environmental performance and durability of construction materials (Uyeda 2009).

For every designer, climatic consideration is essential in order to build an effective and efficient structure (Emmitt and Gorse 2006). In hot and humid region, the climate is uncomfortable and difficult to ameliorate by a passive design (Sh. Ahmad 2008). Builders in the hot and humid climate must be able to address large solar radiation and significant levels of moisture in the ambient air most of the year, along with torrential down pours and high winds, including hurricanes (Baechler 2011).

Lime mortars are more permeable than cement thus allowing building to ‘breathe’ (Lawrence et al. 2007, Banfill and Forster 1999). Using lime mortar can reduce stone decay; saving weaker stone such as sandstone and limestone from the harmful effects of thermal and moisture movement such as freezing and thawing cycles. Walls built with lime mortar have been shown to have an increased tolerance to degradation (Hughes et al. 2003).

2.13.1 Climatic Influences on the Hydraulic Lime and Portland Cement Mortar Performance

The influence of geographical location and climatic conditions are primary design parameters (Forster and Carter 2011). The appropriate selection of materials for use in a specific environment will determine its longevity and performance. Lime mortars have been used globally for millennia and regional techniques and manufacture processes have developed to enable satisfactory use (Mallinson and Davies 1987). In northern climates, the use of lime is inhibited by excesses in temperature and associated freeze and thaw. In high humidity environments carbonation reactions can become dormant. This is reflected in work by Ward-Harvey (2009) who argued that it is an important consideration because the local climatic conditions vary considerably and materials perform differently according to climatic exposure.

Climatic conditions cause stress to building through temperature variations (heat and cold), intensity of solar radiation, atmospheric gases, humidity, rainfall and wind (Dimoudi 2001). Furthermore, environmental conditions will vary according to direction and position of the structure such as north and south elevations which may affect its exposure to phenomenon such as driven rain (Tanabe 2008).

Although lime mortars interact with their environment during the curing process, the environment also plays a major role in the evolution of product, hydration and other mineral compounds (Dotter 2010). Removal of significant amounts of water from these mortars before final set result in insufficient curing conditions and leads to an inferior poorly performing material. A hydraulic lime mortar placed in a high humidity environment will fail to carbonate and therefore not attain its set characteristics (Allen 2003). Those materials will therefore not attain design strength or durability characteristics. The efficacy of formation plays a significant role in determining strength.

Many variables affect the hydration of natural hydraulic lime mortars such as chemical composition of mortar, temperature and relative humidity of mixing and curing conditions. Mortars that are being exposed to high temperature exhibit accelerated hydration and non-uniform distribution of hydration products thus generating a great porosity and an increase of the compressive strength at early age. These favourable conditions decrease with longer term development (Gesoglu 2010).

Al-Ani et al. (1988) have shown that improper curing results in a variety of undesirable effects such as lower strength, scaling, cracking and low resistance to weathering. Their work set out to determine the influence of curing on partially exposed high-strength concrete in hot climates. Bushlaibi (2002) found that high strength concrete is adversely affected by hot dry environments in a similar manner to normal-strength concrete due to excessive moisture evaporation and badly dispersed hydration products resulting from high curing temperatures (Figure 2.23). Using mortar in hot countries with changeable humidity conditions (especially low humidity) results in rapid hydration of the mortar. Therefore, the strength and durability of mortar will decrease and tendency of cracking will increase.

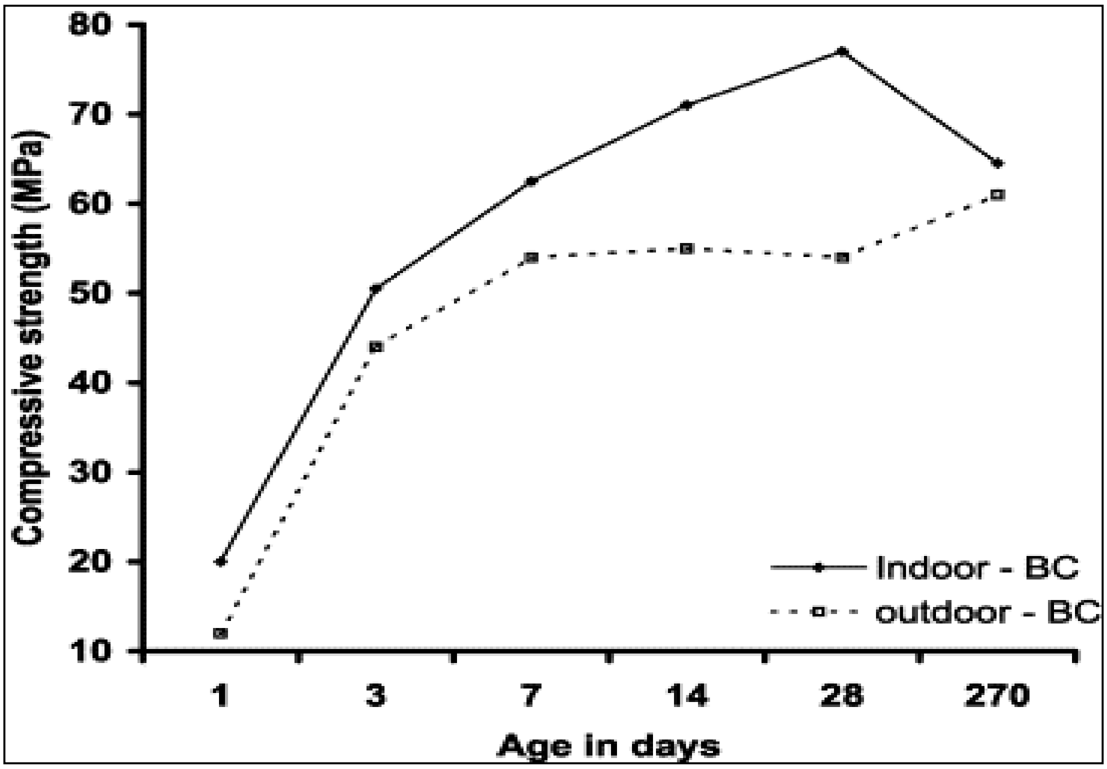


Figure 2.23: Compressive strength development of burlap-cured samples (Bushlaibi and Alshamsi 2002)

As been discussed by Schroder and Ogletree (2009), the high temperature during curing may cause high stresses in new applied mortar that interrupts the carbonation process. Several investigators reported that high temperatures improve the strength at early age (Ezziane et al. 2007). However, if the exposure continues, the arrangement of an important number of formed hydrates cannot satisfactorily occur and engendered ultimate strengths. This behavior has been termed the ‘crossover’ effect (Carino 1994). This is associated with the more dense precipitates being deposited at elevated temperature forming a barrier for ion diffusion. This in turn causes an in-homogeneity in the microstructure and significantly reduces strength (Bakharev et al. 1999).

2.13.2 Relative Humidity (RH)

Environmental conditions can significantly influence the set characteristics and performance of lime mortars. Relative humidity and temperature specifically, influence both hydration and carbonation set reactions with the formation of hydrates determining the mineralogical composition and the ultimate strength and stability of the matrix (Dotter 2010, Taylor 1997, Hewlett 2004).

Hydraulic lime mortars placed in a high humidity environment are understood to exhibit lower rates of carbonation and may not readily attain their full set characteristics due to the potential for high and sustained moisture contents (Allen 2003). The wide scale adoption of non-Portland Cement alternative binders (including NHL) in emerging markets may be hindered by performance and behavioural uncertainty associated with high humidity conditions and equally so by the slow rates of initial set in such materials (Pavia 2008, Ball et al. 2009, El-Turki et al. 2007, Ball et al. 2010).

2.13.3 Hot Climate

Hydraulic lime mortars exposed to elevated temperatures and optimal moisture contents should follow similar hydration kinetics to that associated with Belite (β-C_2S) cements (Hewlett 2004), and exhibit accelerated precipitation of products of hydration (Desai et al. 2011, Forster 2004a). The importance of the carbonation reaction in hydraulic limes cannot be underestimated. Carbonation in simplistic terms is the conversion of $Ca(OH)_2$ into calcite via a chemical reaction with atmospheric carbon dioxide. The extent and rate (kinetic) of the carbonation process are also affected by physical parameters of the masses (porosity/permeability) and by the practical curing and exposure conditions such as carbon dioxide concentration, humidity, temperature etc. (Pacheco Torgal et al. 2012).

Extreme climatic conditions such as in the Arabian Peninsula may lead to limitation of the carbonation and curing process. Schroder and Ogletree (2009), discuss these issues indicating that the high temperature during curing may cause high stress in newly applied mortars that interrupts the carbonation process The region is an arid desert and borders to the sea which causes a great variations between day and night temperature.

The Arabian Peninsula receives very little annual rainfall and best classified as saline ‘severely hot’ and ‘hyper arid’ (Walker 2002). In Arabian Peninsula, climate is governed by direction of the wind, where the northern region is more extreme; hot and dry during the day and extremely cold during the night compare to southern part that is less seasonal (warn and humid) (Department of Environment 1980). Due to the absence of cloud, the region has prolonged and intense solar radiation.

2.14 Geographical Conditions: High Temperature & High Humidity Regions

Hot and humid regions are situated close to the Equator. They extend to 23.5° latitude North and South (23.5°S - Tropic of Capricorn and 23.5°N - Tropic of Cancer) with a predominance of a general high sun position, lack of seasonal variations and seasonal pattern dominated by periods of high rainfall (Hyde 2000, Ahrens 2013). Many hot and humid countries are associated with developing countries (Hyde and Rostvik 2008). Modern South-east Asian cities such as Hong Kong, Singapore, Bangkok, and Kuala Lumpur have developed with rapid construction growth in the last thirty years (Cheng et al. 2005). This is associated with economic growth accompanied by rapid urbanization (Kubota et al. 2009). Figure 2.24 illustrates the high temperature & high humidity regions (AFP 2012).

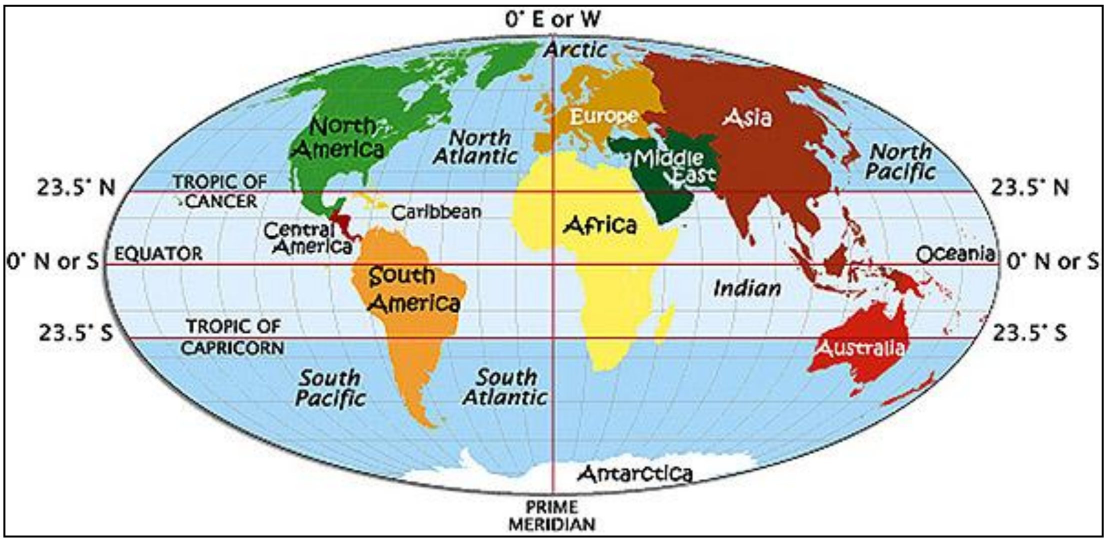


Figure 2.24: High temperature & high humidity regions (AFP 2012)

2.14.1 Climate Background

This region receives more than 150mm of annual precipitation. The nature of the rainfall is characterized by (i) 19.5°C higher wet bulb temperature for 3,000 or more hours during the warmest six consecutive months of the year; (ii) 23°C higher wet bulb temperature for 1,500 or more hours during the warmest six consecutive months of the year (Reeder 2010). Other climates associated with these conditions are Central and South America, Central Africa, Micronesia and South-east Asia. The hot and humid climates (temperature and humidity) of Kuala Lumpur, Malaysia are shown in Figure 2.25 and Figure 2.26, and graphically illustrate the aforementioned situation.

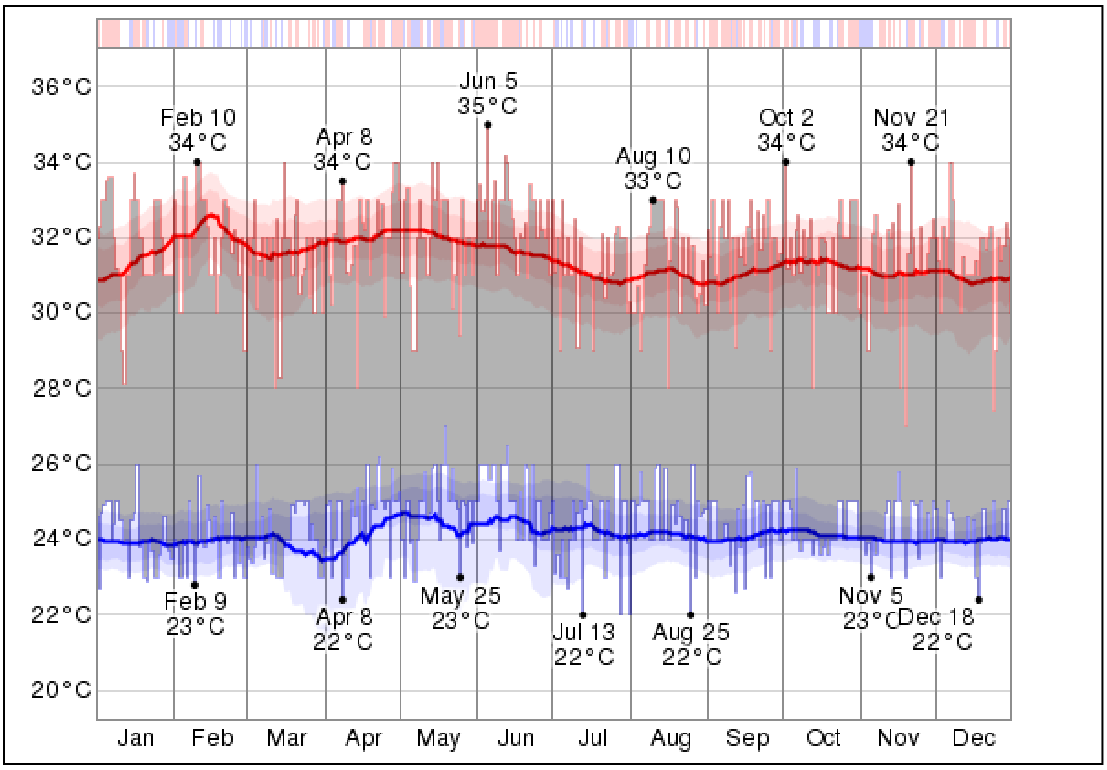


Figure 2.25: Average temperature at Kuala Lumpur International Airport (KLIA) in 2012. The daily low (blue) and high (red) temperature during 2012 with the area between them shaded gray and superimposed over the corresponding averages (thick lines), and with percentile bands (inner band from 25th to 75th percentile, outer band from 10th to 90th percentile). The bar at the top of the graph is red where both the daily high and low are above average, blue where they are both below average and white otherwise (Diebel and Norda 2013).

These regions are warmer, and the atmosphere contains a great deal of energy and therefore the potential hold much more moisture (Shonk 2013). A high humidity value precludes the effectiveness of evaporative cooling, increasing discomfort to the inhabitants (Hyde 2000). This inability for moisture to readily evaporate also has a significant influence on the performance of the materials and structures. A significant example of this is internal condensation (i.e. mildew) (Odom and Dubose 2000). Humidity is an important factor in personal comfort conditions. Hot and humid days can feel even hotter due to the reduction in the potential evaporation discouraging evaporation of ‘sweat’ from a person's skin. Hot and humid regions have significant diurnal elevations of vapour with the rising temperature (Givoni 1998). This is due to high evaporation from the vegetation and from the moist of the soil.

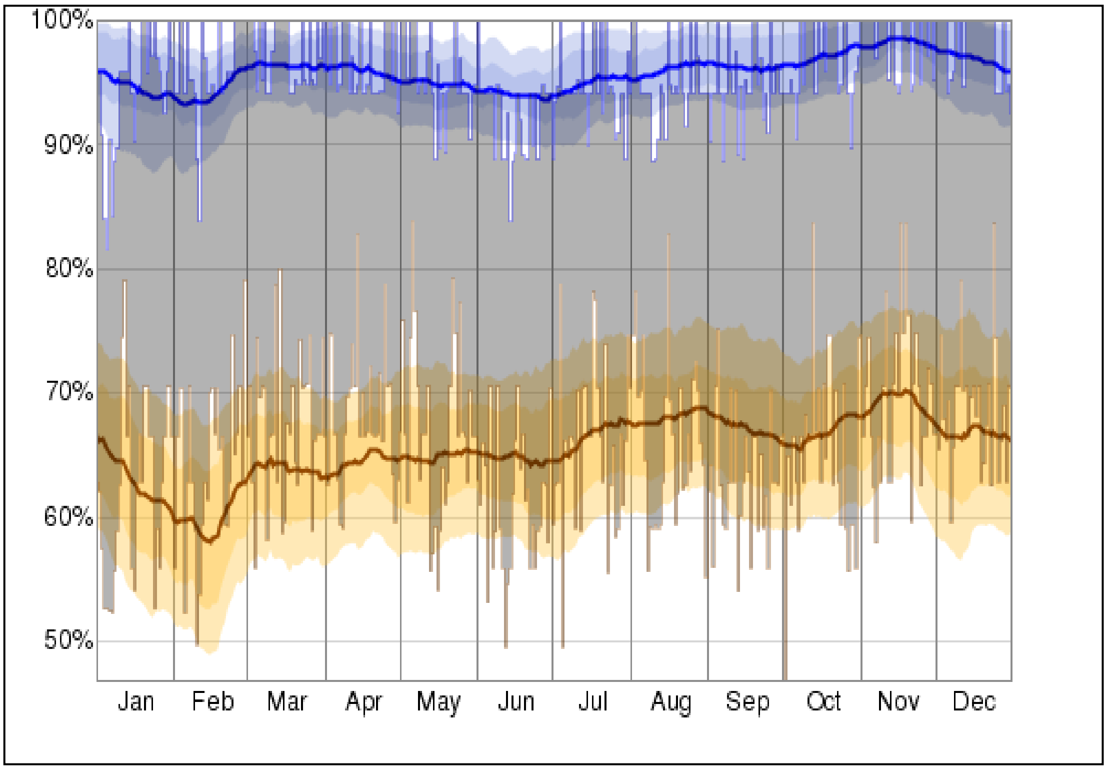


Figure 2.26: Average humidity at Kuala Lumpur International Airport (KLIA) in 2012. The daily low (brown) and high (blue) relative humidity during 2012 with the area between them shaded gray and superimposed over the corresponding averages (thick lines), and with percentile bands (inner band from 25th to 75th percentile, outer band from 10th to 90th percentile) (Diebel and Norda 2013).

2.14.2 Atmospheric Carbon Dioxide Concentrations

The average atmospheric carbon dioxide in Malaysia is around 475-510 ppm (Yau et al. 2012). However, the value could be higher in urban and industrialized location (George et al. 2007). Carbon dioxide concentration also is high in paddy field area; around 895 ppm due to high nitrogen content in soil (Weerakoon et al. 1999).

2.15 Modification of NHL Mortar Mix and Formulation

Mix design and specification can be increased in complexity to achieve better mortar performance. Additives and admixture agents have been employed to modify the properties of hardened mortars and concrete. In addition, the use of aggregate blend is also common to achieve the desired grading and physical characteristics.

Modification is not new. The ancient Chinese were known to have used sticky rice (Liu 2000) and the Romans used animal fat, milk and blood in their mortars (Bridge 1992). It is probable that the early use was utilized by workmen who serendipitously found that the addition enhanced the mortar properties.

Polymers are often mixed with fillers in order to produce a new class of materials, termed polymeric composites. These combinations of materials lead to the new desirable properties. Mineral fillers are added into the polymer matrix to improve mechanical properties and surface hardness (Mihajlović et al. 2009).

2.15.1 Calcitic Fillers

Research has been conducted on calcite as filler. Benachour et al. (2008) attempted to identify the maximum amount of filler which may be added to cementitious materials without performance loss. Performance is quantified here as being related to various micro-structural (density, porosity, pore size distribution, capillary absorption, Klinkenberg effect), and mechanical (Young's modulus, compressive and flexural strengths). In addition, the influence of these fillers upon durability (intrinsic gas permeability, drying shrinkage and mass loss) has also been investigated. Results indicate the existence of an optimal performance value and a high effect of filler addition. In particular, for high filler quantities, total porosity increases (Benachour et al. 2008).

Benachour (2009) investigated the effects of a high calcite filler additions into mortar focusing upon its micro structure and freeze/thawing resistance, as a significant indicator of durability indicator. Guemmadi et al. (2009) substituted a certain percentage of Portland cement with limestone fines in attempts to enhance for compressive strength, but primarily to reduce cement consumption and therefore enhance economic viability. The results were illustrated in Figure 2.27. It was later concluded that an addition of finely ground limestone filler (up to 18%) gives better strength with the same cement content. It additionally, reduced the cost of concrete with the same target strength (Guemmadi et al. 2009).

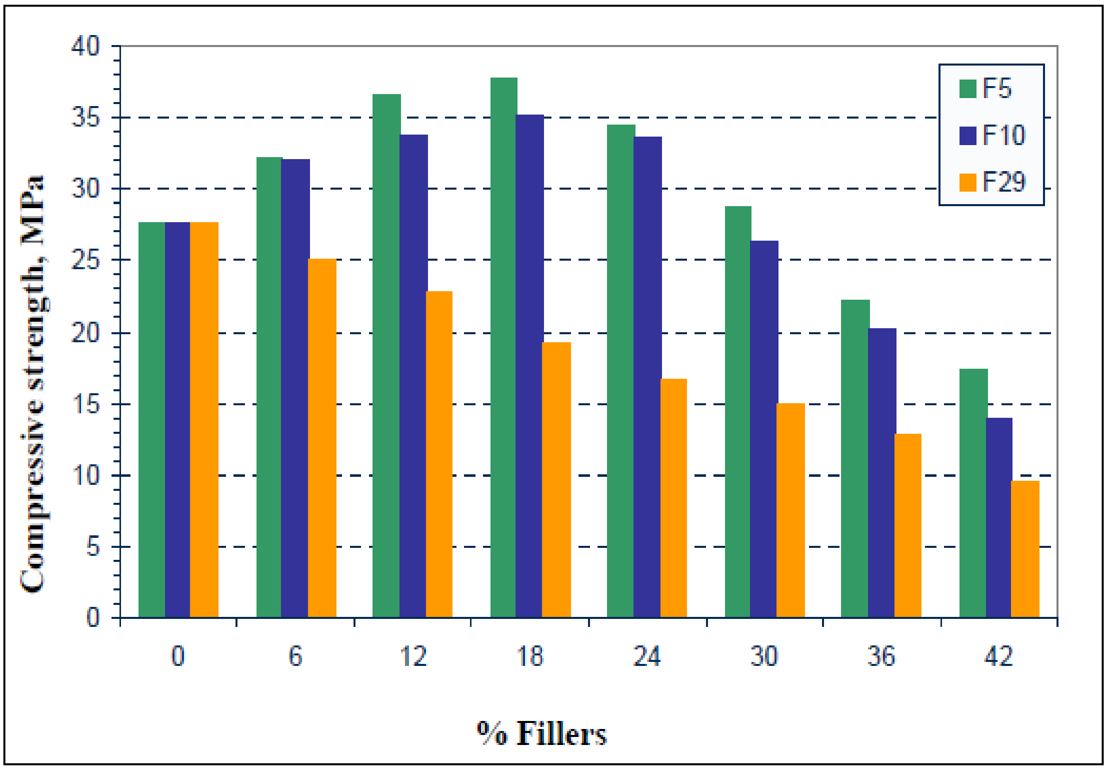


Figure 2.27: Influence of filler concentration on 28 days compressive strength. The fines were designated by F5, F10 and F29, respectively with the fillers diameter of 5 µm, 10 µm and 29 µm (Guemmadi et al. 2009).

2.16 Lime Mortar Modifications Utilising Calcitic Fillers

The industrial preparation of dry constituents can facilitate the introduction of admixtures, binders and aggregates with different particle size distributions. The addition or substitution of industrial by-products aggregates such as marble dust (MD), metakaolin (MK) and crushed limestone can contribute to performance, sustainability and economy of the mortars since binder is the most expensive component of mortar and concrete. Modification of mortars aggregate can alter the characteristics and microstructure (Faria and Silva 2013).

The addition of calcitic aggregates into lime mortars has many historic precedents and these components are often found in many historic mortars (Hughes et al. 2003, Gibbons et al. 2003). Evidence suggests that inclusions of calcite (i.e. crushed limestone or seashells) are perceived to promote crystal growth and the conversion of Portlandite into calcite ($CaCO_3$) during the setting process thus helping to develop early stage strength (Forsyth 2007, Yoon et al. 2003, Yoon et al. 2004, Liang and Wang 2013, Yang et al. 2010). Finely ground calcite additives in the aggregates have been shown to improve the rate of carbonation and prevent strength loss (Taylor 1997, Skoulikidis et al. 1995, Skoulikidis et al. 1996).

Ground limestone ($CaCO_3$) has been used as a replacement of OPC, and its effect on the hydration of OPC has been studied intensively (Hawkins et al. 2003, Li et al. 2009, Pera et al. 1999, Thomas et al. 2010, Guemmadi et al. 2009). These studies have indicated positive effects of the addition of $CaCO_3$ on the hydration of cement and strength development of hardened concrete, especially its accelerating effect on the rate of the hydration.

Fillers can be naturally available materials or synthetic (processed inorganic mineral) materials (Moosberg-Bustnes et al. 2004). The most important factors are the uniform properties and fineness (particle size) (Korjakins et al. 2012). Neville (2002) suggested that fillers must not increase the water content unless the filler was used with water reducing admixture.

The characteristics of mortars comprising several components are influenced by both the particle size distributions and the chemical-mineralogical compositions of the component materials. It is evident that an increase in mass of the mortar is noted within the carbonation process as the diffused carbon dioxide transforms portlandite into calcite (Dheilly et al. 2002). It has been suggested that the presence of calcitic materials aids carbonation as it is typically a relatively porous particulate and therefore facilitates carbon dioxide diffusion through the fresh mortar. In contemporary work, calcitic aggregate additives are used by specifiers and contractors to enhance the initial set in limes in high humidity environments. This is especially common on the West Coast of the UK, well known for high rainfall and low potential evaporation (Hall et al. 2010).

2.16.1 The Influence of Fillers on Strength Development

In their research on lime-based mortars for masonry repair and more specifically their mechanical behaviour, Lanas and Alvarez-Galindo (2006) found the use of calcareous aggregates has a great affect upon the strength when compared to siliceous aggregates (Figure 2.28). The grain size distribution of the aggregates was identified as the most important attribute in relation to aggregate characteristics. It was later concluded that the type and shape of the aggregate influence the mortar strength with angular limestone most improving the strength. The lack of discontinuity between the binder matrix and the aggregate of the same nature improves the strength, as well as a good packing of the aggregate with angular edges.

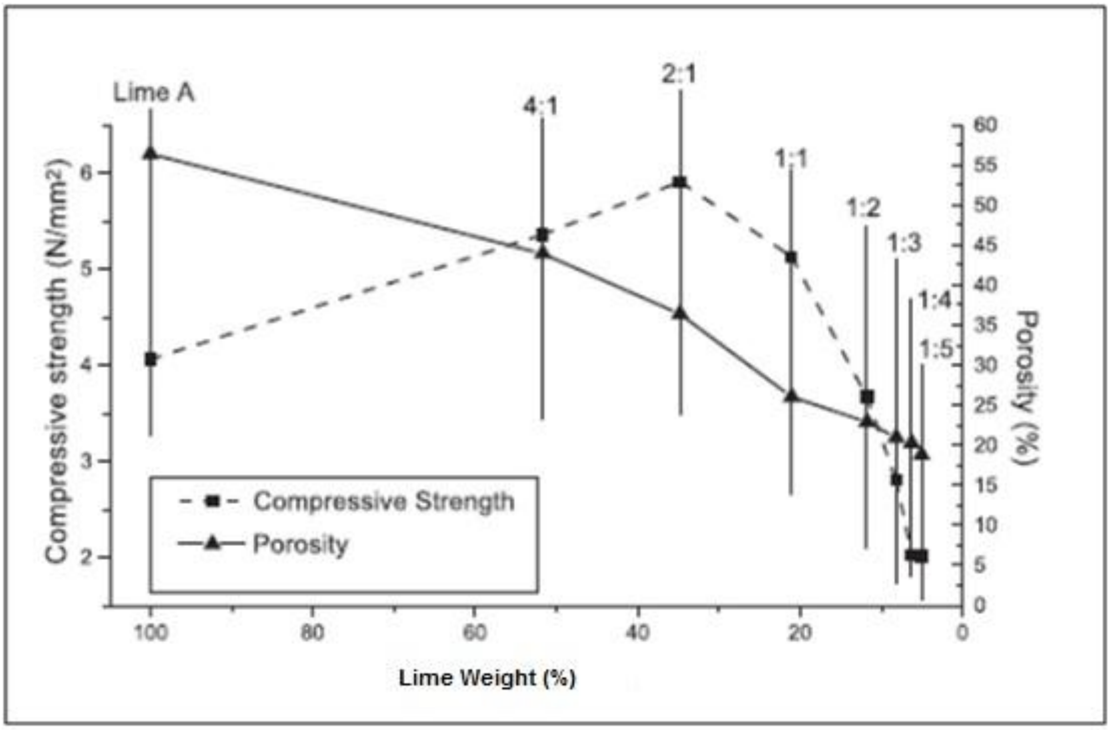


Figure 2.28: Porosity and compressive strength versus percentage of mortars specimens with calcitic aggregates tested after 365 days. B/Ag ratios are expressed on top of points (Lanas and Alvarez-Galindo 2006).

2.17 Seeding

Seeding is considered as nanotechnology in civil engineering (Gopalakrishnan et al. 2011). Seeding microstructures has been long recognized as a method for either improving microstructures or to increase the rate of phase formation (Badger et al. 2002). Therefore, seeding is applied to modify the kinetics and microstructure development.

2.17.1 Seeding Materials on Chemical Reactions

It is hypothesized that the establishment of crystal architecture that catalyses the precipitation of Ca^{2+} ions into growth of calcium carbonate (Gebrehiwet et al. 2012). This concurs with work by various investigators such as Hewlett (2004) and Forster (2004b) that established the influence of temperature and super saturation of Ca^{2+} ions in the liquid phase upon hydration kinetics. Forster et al. (2013) described the Ca^{2+} reaction during seeding;

> *"The rate of hydration of calcium silicates is restricted by an impermeable hydrate layer of Ca*$^{2+}$ *ions that surrounds the grain potentially leading to a temporary period of dormancy. The addition of calcitic material may minimize the effect of the dormancy period leading to an accelerated deterioration of the Ca*$^{2+}$ *ion layer as they are readily utilized in the formation of calcite. This is potentially responsible for the reactivation of the hydraulic phase dissolution and precipitation activity".*

The development of early stage products of hydration have been previously associated with an impedance to carbon dioxide diffusion in lime mortars therefore inhibiting carbonation (Radonjic et al. 2001). It was later concluded by Ezziane et al. (2007) that the seeding processes can positively influence the mortar hydration and minimizes disorders caused by the temperature rise.

2.17.2 Contemporary Researches on Seeding

Skoulikidis et al. (1995) showed that presence of additional calcium carbonate as crystallization seed (autocatalysis) in the mortar enhances the rate of carbonation. Seeding with 6% finely ground calcite has been shown to improve the rate of carbonation. This conforms with grain boundary strengthening theory based upon the Hall–Petch equation (Equation 2.2) (Skoulikidis et al. 1996).

Shetty (2013) discusses seeding as unconventional method for making high strength concrete. Sato and Diallo (2010) argued that the accelerating effect of $CaCO_3$ is an advantage and studies should be conducted to maximize its effect. In his study on influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement, Thomas et al. (2009) found that the seeding effect of C−S−H also provides a new explanation of the hydration-accelerating effects of various forms of reactive silica because these additives form C−S−H by reacting with aqueous calcium ions released by cement dissolution.

Osman et al. (2004a) highlighted the understanding the rheology of composites is not only essential for optimizing their compounding and processing but also for achieving the targeted end properties. The perceived beneficial nature of seeding is not understood mechanistically. However, several potential reasons have been postulated that could lead their serendipitous addition to have inadvertently enhanced performance. In contemporary work, calcitic aggregate additives are used by specifiers and contractors to enhance the initial set in limes in high humidity environments. This is especially common on the West Coast of the UK, well known for high rainfall and low potential evaporation (Hall and Hoff 2012).

2.18 Calcium Carbonate Polymorphs

The carbonates group contain approximately 150 minerals with plane triangular $(CO_3)^{2-}$ anionic groups linked together by cations (Ming 2006). The carbonate minerals are easily distinguished from other minerals classes (see Table 2.9) by its smoothness, unique colours and reaction with dilute hydrochloric acid (HCl). In this carbonates group, Battey and Pring (1997) listed 70 species with calcite, dolomite and siderite being the most abundant.

Table 2.9: Carbonate group (Blackburn and Dennen 1994)

Carbonate Group		**Colour**
Calcite Group		
Calcite	$CaCO_3$	Colourless or white, may be brownish, red, blue, green or black
Magnesite	$MgCO_3$	Colourless, white greyish or yellowish brown
Siderite	$Fe^{2+}CO_3$	Yellowish brown or brown
Rhodochrosite	$MnCO_3$	Pink of various shades
Smithsonite	$ZnCO_3$	Grey-white to dark grey; also apple-green or bluish green
Dolomite	$CaMg(CO_3)_2$	Colourless, or white to cream and yellow brown. Sometimes pale pink
Ankerite	$CaFé(CO_3)_2$	White. Yellow, yellow-brown
Aragonite Group		
Aragonite	$CaCO_3$	All are colourless in transmitted light, with marked variation in relief on rotation in plane polarized light.
Witherite	$BaCO_3$	
Strontianite	$SrCO_3$	
Cerussite	$PbCO_3$	
Monoclinic carbonates with $(OH)^-$		
Azurite	$Cu_3(OH)_2(CO_3)_2$	Translucent, pale blue
Malachite	$Cu_2(OH)_2CO_3$	Translucent green to yellow green
Hydrated carbonates		
Thermonatrite	$Na_2CO_3.H_2O$	Grey-white or yellowish. Colourless when pure
Troma	$Na_3H(CO_3)_2.2H_2O$	

2.18.1 Polymorphic Transformation

There are three formations of polymorphs of calcium carbonate; calcite, aragonite and vaterite (Brezonik and Arnold 2011). Calcite is usually the primary polymorph formed during carbonation, although vaterite and aragonite may also produced depending on super saturation process (Rochelle and Milodowski 2004). Calcite is the most thermodynamically stable, aragonite is mainly found in the biosynthetic calcium carbonate such as shells and corals and veterite (the most unstable polymorph) seldom occurs in natural fields, but plays an important role in the calcium carbonate formation from solution (Sawada 1997).

2.18.2 Solution Equilibrium

The chemical equilibriums of the calcium carbonate systems are expressed in terms of the protonation (addition of H^+) of carbonate ion (Sawada 1997, Kotz et al. 2009, McElroy 2002, Van Balen 2005);

$CO_3^{2-} + H^+ \rightleftharpoons HCO^{3+}$ (Equation 2.4)

$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$ (Equation 2.5)

$H_2CO_3 \rightleftharpoons CO_2 + H_2O$ (Equation 2.6)

$CO_2 \rightleftharpoons CO_2$ (gas) (Equation 2.7)

The formation and hydrolysis of calcium ion;

$Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^-$ (Equation 2.8)

$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$ (Equation 2.9)

The solubility equilibrium of calcium carbonates is given by;

$CaCO_3$ (solid) $\rightleftharpoons Ca^{2+} + CO_3^{2-}$ (Equation 2.10)

2.18.3 Transformation Mechanism

Nebel et al. (2008) enlisted six polymorphs (in decreasing stability) as calcite, aragonite, vaterite, calcium carbonate monohydrate (monohydrocalcite), calcium carbonate hexahydrate (ikaite) and amorphous calcium carbonate (ACC). The unstable polymorphs are able to be transformed into more stable polymorphs such as aragonite or calcite through precipitation (Zhang et al. 2012). Peric et al. (1996) used numerical and stationary point theory to design an experiment on the transformation of aragonite and vaterite into the stable modification calcite. It was hypothesized by Wada et al. (1995) that the adsorption of water soluble polymers should have strong influence on both the rate and the pattern of the crystal growth. Wei et al. (2003) illustrated in Figure 2.29 the mechanism of transformation starting from dissolution of least stable polymorph (veterite) and followed by the crystallization of higher stable polymorph (calcite).

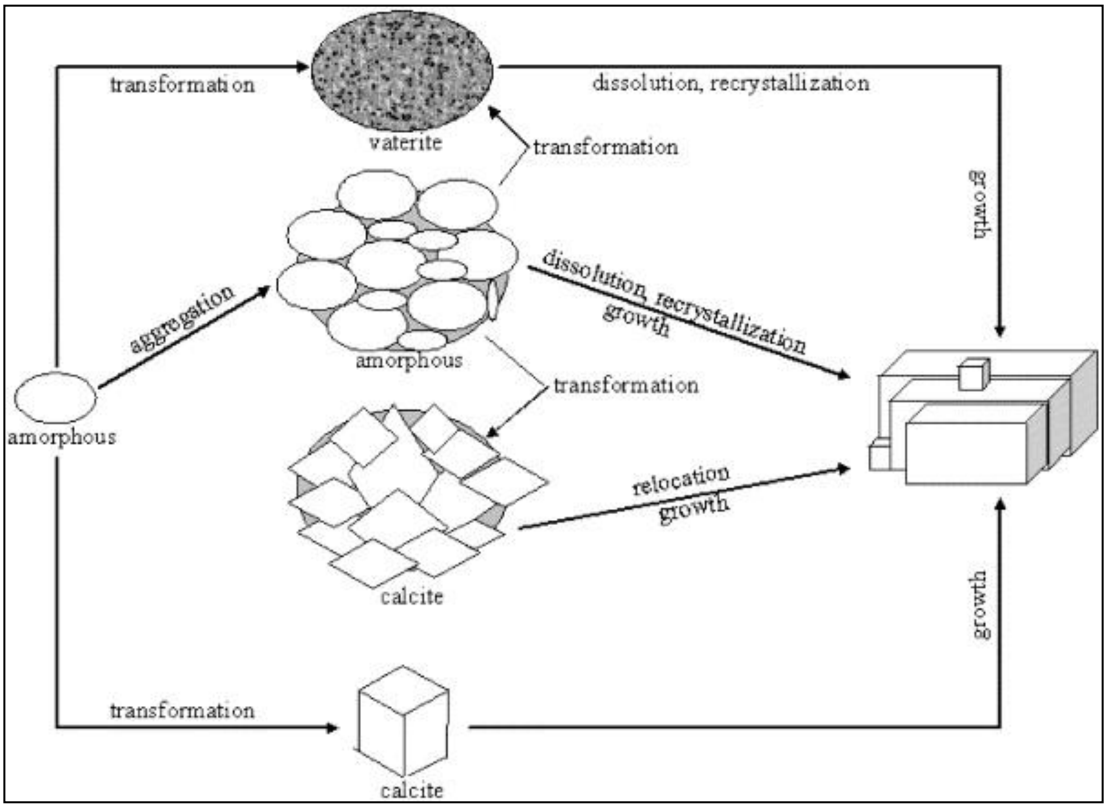


Figure 2.29: Schematic diagram of the transformation of polymorph from amorphous phase to typical calcite (Wei et al. 2003)

2.18.4 Effects on Temperature

The abundance of calcium carbonate formed by homogeneous precipitation are strongly affected by temperature (Chang et al. 1996). Ogino et al. (1987) studied the effects of temperature on calcium carbonate crystalline growth in water (see Figure 2.30) and establish the following observations and conclusion;

> *"Calcite is the dominant polymorph at low temperature. With increasing temperature, the calcite abundance decreases. The predominant polymorph changes from calcite to vaterite and the formation of aragonite was observed at 40 °C. At higher temperatures aragonite is the dominant species. All the crystals are finally transformed into calcite at any temperatures. The mechanism of*

transformation is essentially the same at any temperature. At high temperatures, the polymorphs formed in the meta-stable stage are aragonite and a small portion of calcite".

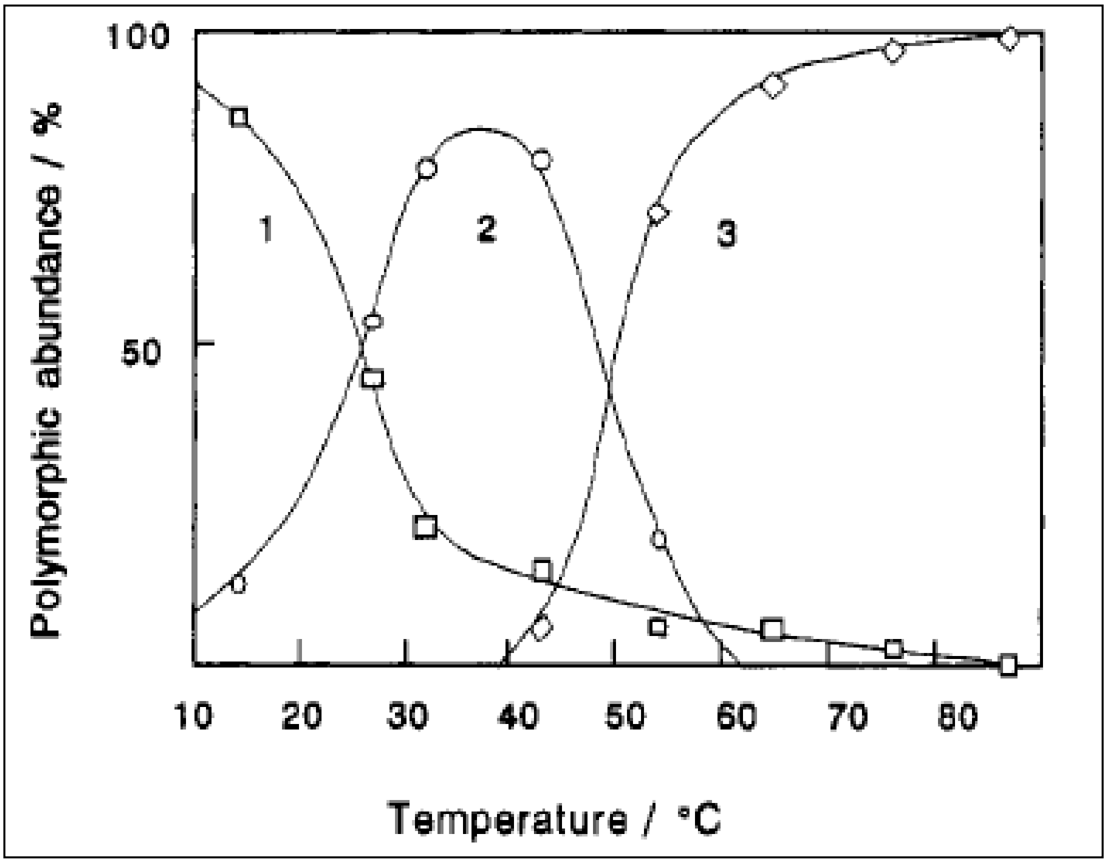


Figure 2.30: The effects of temperature on calcium carbonate crystalline growth (Ogino et al. 1987). ***Note: Curve 1 is calcite, curve 2 is vaterite and curve 3 is aragonite***

2.19 Calcite

Calcite is one of the oldest manufactured powders, while the precipitated calcium carbonate was first created almost a hundred years ago (Osman and Suter 2002). Calcites are usually very crystalline, have a blocky pattern and cleave into rhomb-shaped fragments. Grounded natural calcite is usually micron-sized (for dispersion purposes) with a broad size distribution and irregular shape, in contrast to precipitated calcium carbonate (PCC) (Osman et al. 2004b). According to De Leeuw and Parker (1998), calcite have been the subject research interest in both experimentally and theoretically such as the local density approximation computation, microscopy studies, growth and inhibition rate and morphology changes.

2.19.1 Natural Occurrence

Calcite is frequently found as the main component of sedimentary and metamorphic rocks (Cairncross 2004). Calcite is widely available in limestone, sea shells or chemical precipitation from sea water (Monroe and Wicander 2014). Calcite can be found in the shells of aquatic organisms such as plankton (coccoliths and planktic foraminifera), the hard parts of red algae, sponges, brachiopods, echinoderms, bryozoa and parts of the shells of some bivalves (such as oysters and rudists) (McMullen and Jabbour 2009, Odgers and Henry 2012).

The surface ocean is saturated with respect to both of calcite and aragonite, but direct precipitation of calcium carbonate from seawater does not occur on the ocean surface but at deeper levels, in which the ocean is more saturated (Eby 2004). In freshwater, calcite is precipitated as travertine through evaporation process (Pentecost 2005).

2.19.2 Structure

The structure of calcite can be hard to visualize and is not cubic (Ropp 2013). Its symmetry is modified in three ways; (i) three symmetry axes line up in parallel with cube surface except one axis is on the cube; (ii) orientation changes and (iii) the available space is stretched thus making the cube become distorts (rhombohedra) (see Figure 2.31) (Nesse 2000). Calcite structure is composed of a structure of a carbon (C) atom occupying the centre and surrounded by three oxygen (O) atoms arranged in rhombus triangle linked by cations (Ming 2006). Calcite crystals are generally found in trigonal-rhombohedral but can be found in numerous forms such as obtuse rhombohedra, tabular forms, prisms, or various scalenohedra (Siegesmund and Torok 2011). Blackburn and Dennen (1994) illustrates common forms of calcite as shown in Figure 2.32.

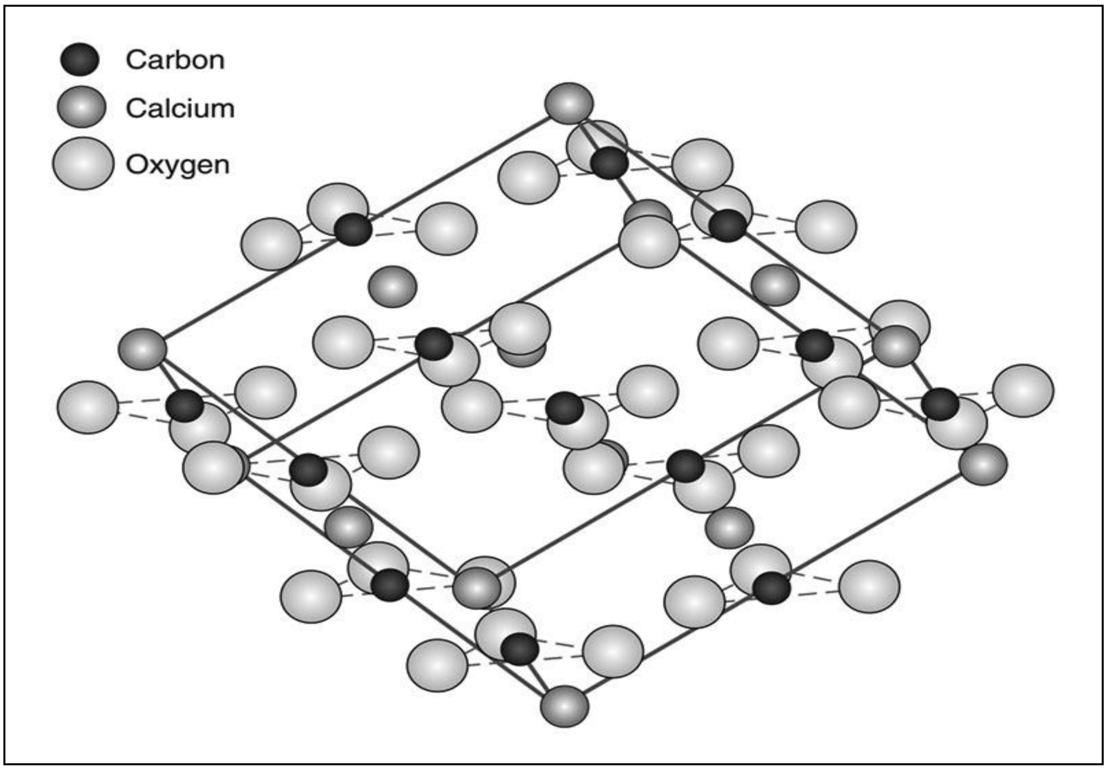


Figure 2.31: Rhombohedra structure of calcite (Shaffer 2013)

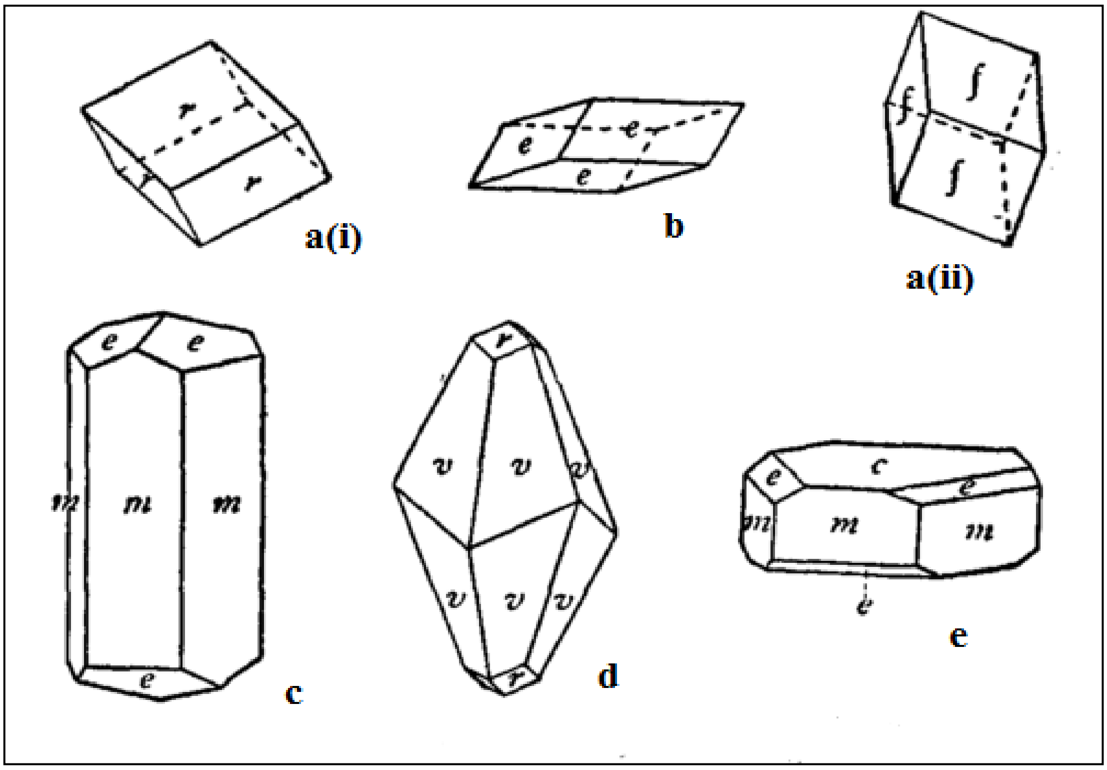


Figure 2.32: Common form of calcite. (a) acute rhombohedral (b) flat acute rhombohedral (c) prismatic (d) scalenohedal (dog-tooth spar) (e) flat rhombohedral (Blackburn and Dennen 1994)

2.19.3 Properties

Calcite is relatively soft with a scratch hardness of 3 on the Mohs scale but Stocks (2003) found that Egyptian calcite might reach Mohs 3.5. The impurities given by the minerals contained in the calcite result in a wide variety of colours i.e. white or translucent, grey, red, orange, yellow, green, blue, violet and brown (Chang et al. 1998). In terms of optical properties, transparent rhombohedron calcite has a strong double light refraction caused by high degrees of birefringence (Corcione and Frigione 2011).

It has been established by Battey and Pring (1997) that the minerals tendency (cleavage) to break smoothly at certain particular planes is driven by the weak bond strength across that area (plane) rather than the directions of the structure. Healy (1999) explained that cleavage planes are always located at higher density atom location thus making cleavage always in parallel to crystal face. Figure 2.33 illustrate a prominent cleavage in most varieties.

Figure 2.33: Blue calcite rhombohedral cleavage (calcite containing niobium)

2.19.4 Acid Test

Calcite like most carbonates will dissolve in most forms of acid. Calcite can be either dissolved by groundwater or precipitated by groundwater, depending on several factors, including the water temperature, pH and dissolved ion concentrations. Although calcite is fairly insoluble in cold water, acidity can cause dissolution of calcite and release of carbon dioxide gas.

In earth science and geology studies, the “acid test” is a quick in-situ investigation to determine calcium carbonate rocks (Winegardner 1995). Methodologically, a drop of dilute (5% to 10%) hydrochloric acid (HCl) is used and formation of bubbles indicate the presence of carbonate minerals (Nichols 2009). The metathesis reaction of calcium carbonate and hydrochloric acid will produce three products; carbon dioxide, salt and water as stated in (Equation 2.11) (Bradley 2002);

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$$

$$\text{acid + calcium carbonate} \rightarrow \text{salt + carbon dioxide + water}$$

(Equation 2.11)

This is an exothermic reaction (Equation 2.12);

$$CaCO_3 + 2H^+ + 2Cl^- \rightarrow Ca^{2+} + 2Cl^- + H_2O + CO_2$$

(Equation 2.12)

King (2005) listed the frequently and infrequently encountered carbonate minerals with their chemical formula and reactions with hydrochloric acid as shown in Table 2.10.

Table 2.10: Acid reaction based on mineral (King 2005)

Mineral	Chemical Composition	Cold Acid Reaction	Warm Acid Reaction
Aragonite	$CaCO_3$	strong	strong
Azurite	$Cu_3(CO_3)_2(OH)_2$	yes	strong
Calcite	$CaCO_3$	strong	strong
Dolomite	$(CaMg)(CO_3)_2$	weak	yes
Magnesite	$MgCO_3$	very weak	weak
Malachite	$Cu_2CO_3(OH)_2$	yes	yes
Rhodochrosite	$MnCO_3$	weak	yes
Siderite	$FeCO_3$	very weak	weak
Smithsonite	$ZnCO_3$	weak	yes
Strontianite	$SrCO_3$	yes	yes
Witherite	$BaCO_3$	weak	weak

2.19.5 Use and Applications

Calcite is also found as fibres, nodules, earth aggregates, stalactites and stalagmites (Bonewitz 2012). The properties of calcite make it one of the most widely used minerals. Because of its harmless properties and inexpensiveness, it has been used for a variety of purposes such as a construction material, filler, flux, cement, abrasive, agricultural soil treatment, construction aggregate, pigment and pharmaceutical.

Recycling of calcitic aggregates, generated by the industries, as alternative raw materials is not a new thing and has been done successfully in a lot of countries. The use of wastes as alternative raw materials in the ceramic industry, which embodies part of the construction industry, can contribute to diversify the offer of raw materials in the production of ceramic bricks and tiles and reduce the costs in a building (Menezesa et al. 2005). However, Filippidis and Georgakopoulos (1992) highlighted the need of chemical and mineralogical compositions properties studies based on concern to the construction industry and even to health and the environment.

2.20 Oyster Shells

As a key species, oysters provide habitat for many marine species (Raj 2008). Crassostrea and Saccostrea live mainly in the intertidal zone, while Ostrea is sub tidal zone (Lam and Morton 2004). The hard surfaces of oyster shells and the nooks between the shells provide places where a host of small animals can live (Hopkins 2008). The quality of oysters is strongly influenced by the marine surroundings due to the its filter-feeding nature (Cruz-Romero et al. 2007). Hundreds of animals, such as sea anemones, barnacles and hooked mussels inhabit oyster reefs (Kidwell 2007).

Chemical analysis, X-ray diffraction analysis (XRD), measurement of specific surface by Brunauer–Emmett–Teller (BET) theory and microstructure analysis by scanning electron microscope (SEM) were utilized in investigating the physical and chemical properties of oyster shell (Yoon et al. 2003).

2.20.1 Physical Characteristics

Oyster shells consists of both calcite and aragonite depending on the organism's proteins content (see Figure 2.34) (Choi and Kim 2000). Zhong et al. (2012) enlisted beneficial physical characteristics of oyster shells as high amount of micro pores, high strength, light in mass, low density, low heat conductivity and resistance to weathering. The simplified oyster shell physical characteristics are shown in Table 2.11 (Weismantel 1999).

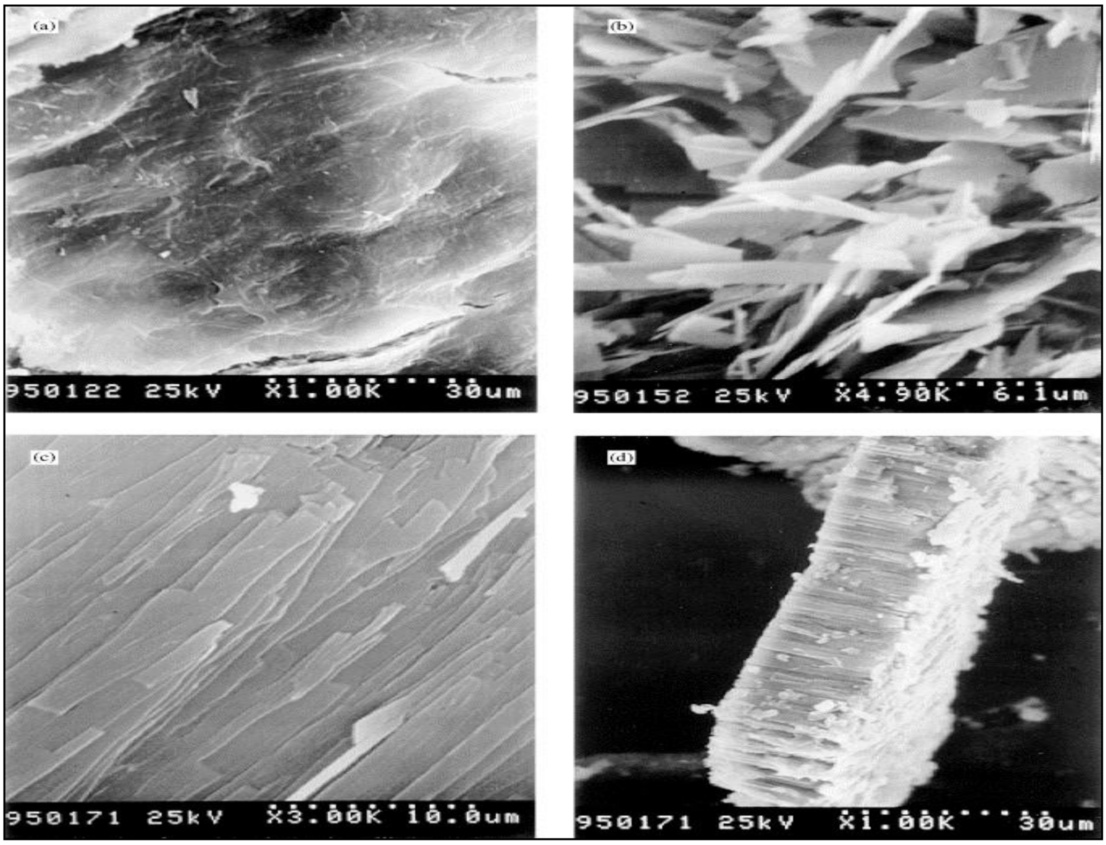


Figure 2.34: SEM images of oyster shell: (a) outer layer - calcite (b) center layer - calcite (c) inner layer - calcite (d) myostracum – aragonite (Choi and Kim 2000)

Table 2.11: Oyster shell physical characteristics (Weismantel 1999)

Hardness (Mohs)	3.0
Refractive Index	1.658
Specific Gravity	2.65 – 2.72
Colour	White to off-white
Particle size (μm)	0.07 -200

2.20.2 Chemical Characteristics

Chemical and microstructure analyses reveal that oyster shells are predominantly composed of calcium oxide (CaO) (Liang and Wang 2013). Table 2.12 shows the chemical composition of oyster shells (Lee et al. 2008).

Table 2.12: Physical and chemical properties of oyster shell (Lee et al. 2008)

Analytical items	**Mean (*n* = 6)**	**Standard deviation**
pH	9.8	0.83
Electrical Conductivity (dS m^{-1})	18.9	3.89
Water soluble NaCl (g kg^{-1})	2.7	0.58
Organic matter (g kg^{-1})	13	2.8
Total concentration (%, wt wt^{-1})		
Aluminum oxide, Al_2O_3	0.42	0.05
Calcium carbonate, $CaCO_3$	95.9	6.25
Magnesium oxide, MgO	0.65	0.09
Sodium oxide, Na_2O	0.98	0.19
Phosphorus pentoxide, P_2O_5	0.20	0.04
Silicon dioxide, SiO_2	0.69	0.08
Moisture content (%, wt wt^{-1})	4.5	0.98
Bulk density (g cm^{-3})	1.03	0.12

Typically oyster shells consist of a β-anti-parallel structure with dominant aragonite and secondary calcite (Lee et al. 2011). However, investigations undertaken by Yoon et al. (2003) and Yoon et al. (2004) found that the mineral phase of calcium carbonate is calcite (see Figure 2.35). It was observed that shell powder became calcium oxide (CaO) after a heat treatment (pre-treatment to eliminate bacteria). It is believed that the formation of calcite or aragonite depends on the shell morphology and the type of species present.

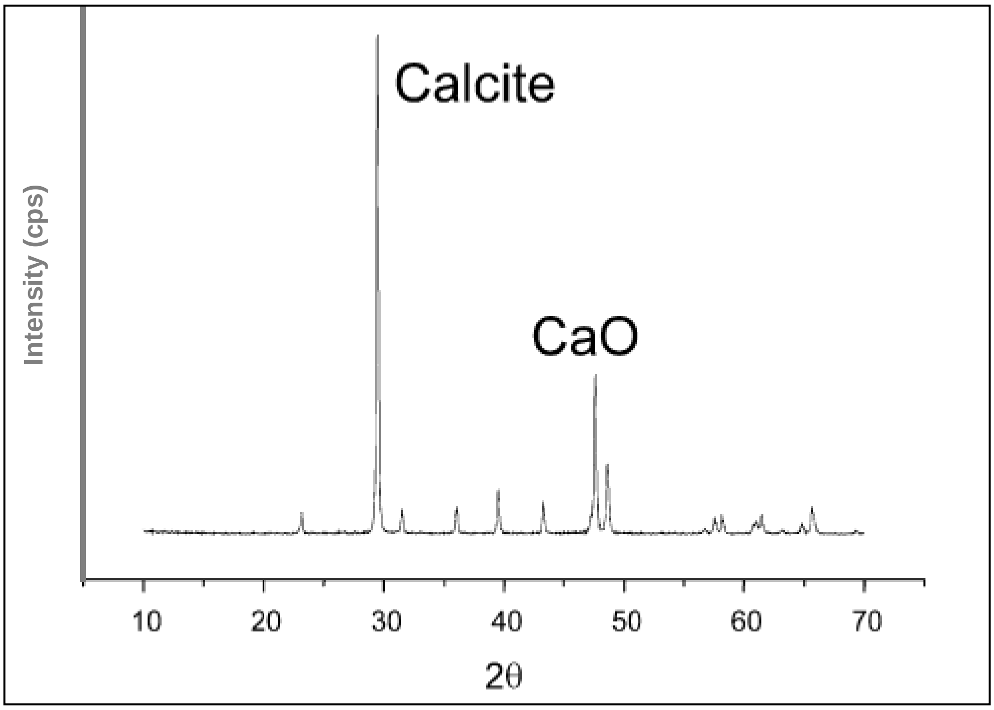


Figure 2.35: XRD pattern of oyster shell (Yoon et al. 2003)

2.20.3 Contemporary Use

Oyster shells are a problematic waste product from marine-culture and cause a major disposal problem in coastal regions of Far East Asia because a large amount of oyster shell is produced every year (Liu et al. 2010). The oyster shell waste has led to severe problem of solid waste pollution. Recycling of these materials has arisen as an imminent issue in marine-culture areas. The ideal solution is to convert the waste oyster shells to a product that is both beneficial and economically viable.

Oyster shells, especially the valve section is highly calcified (Miller et al. 2009). Due to this, it has a high potential to be used as a liming material in agriculture, construction and industry. A number of oyster shell wastes are used as source of calcium carbonate in fertilizers and chicken feed, but the use is limited. Oyster shell is positively applied in certain industries such as soil treatment, sand compaction and aggregate for cement and road construction, and removal of phosphate species from waste waters (Tongamp et al. 2008).

2.20.4 Construction Aggregates Substitution

Previous research has been undertaken into oyster shell waste as construction materials (Jegatheesan et al. 2009, Barros et al. 2009, Yang et al. 2010, Liang and Wang 2013). Evaluation of the physical properties of the oyster shell has been undertaken (California Bearing Ratio (CBR)) value of surface materials and oyster shell processing methods (Yoon et al. 2003). Studies which set out to determine the possibility of oyster shells as aggregates, Yoon et al. (2004) found that there was no significant reduction in the compressive strength of the mortars containing small particles of oyster shell instead of sand. This was later supported by Yang et al. (2010) in which the effect of substitution ratio (SR) of oyster shells on the compressive strength at 28th day was not detrimental. When the substitution of greater amounts was undertaken the strength decreased over time long-term (see Figure 2.36).

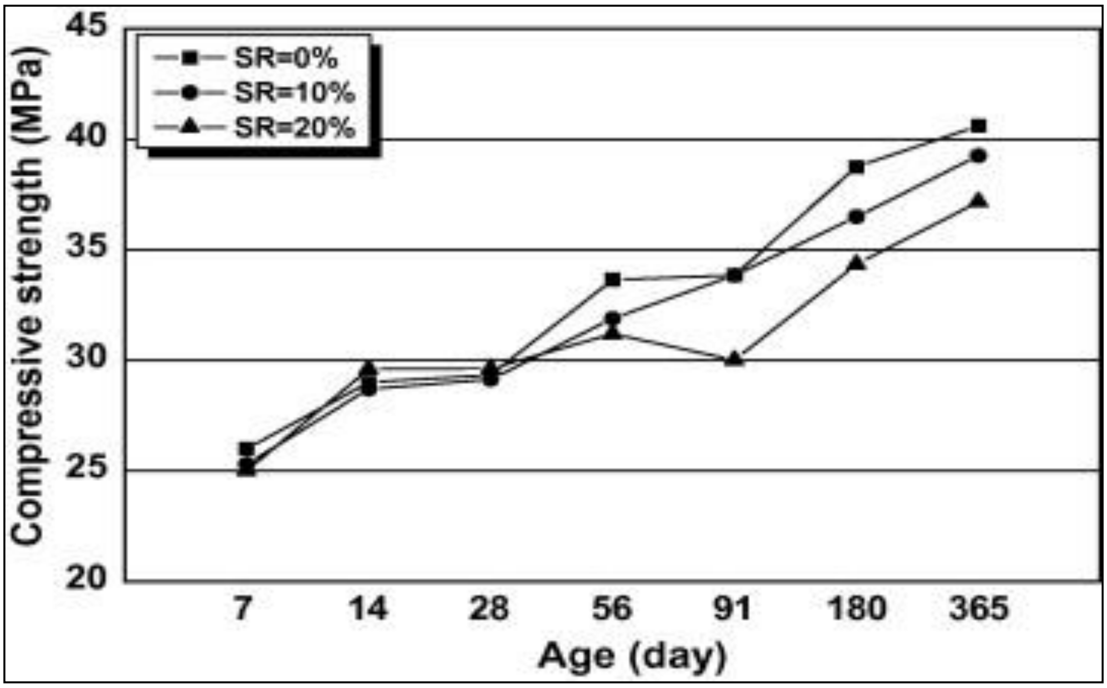


Figure 2.36: Relationship between compressive strength and age with substitution ratio (Yang et al. 2010)

2.21 Limestone

Like most other sedimentary rocks, limestone is primarily composed of grains. Limestone often contains variable amounts of silica in the form of chert (chalcedony, flint, jasper, etc.) or siliceous skeletal fragment (sponge spicules, diatoms, radiolarians), and varying amounts of clay, silt and sand (terrestrial detritus) carried in by rivers (Burek and Stilwell 2007). However, some limestones do not consist of grains, and are formed completely by the chemical precipitation of calcite or aragonite, i.e. travertine (Gueguen and Palciauskas 1994). Secondary calcite may be deposited by supersaturated meteoric waters (groundwater that precipitates the material in caves). This produces speleothems, such as stalagmites and stalactites. Another form taken by calcite is oolitic limestone, which can be recognized by its granular (oolite) appearance (Dimes 2011).

The primary source of the calcite in limestone is most commonly marine organisms (Myers 2007). Some of these organisms can construct mounds of rock known as reefs, building upon past generations. Below about 3,000 meters, water pressure and temperature conditions cause the dissolution of calcite to increase nonlinearly, so limestone typically does not form in deeper waters (Trewin and Davidson 1999). Limestone may also form in both lacustrine and evaporite depositional environments (Spencer and Pearthree 2008).

2.21.1 Concrete Strength Optimizer

The use of limestone fillers as additions in concrete has grown in recent years because they present several advantages over ordinary cements. The use of limestone in a form of ground calcium carbonate (GCC) can improve concrete density, surface smoothness, physical properties and esthetical values to suit architectural applications. It is increasingly being used in applications, such as precast concrete products (block paving, paving slabs, roof tiles), ready mixed concrete and self-compacting concrete (SCC) (Paulou 2003).

In addition, pervious concrete has been increasingly used to reduce the amount of runoff water and improve the water quality near pavements and parking lots. However, due to the significantly reduced strength associated with the high porosity, pervious concrete mixtures currently cannot be used in highway pavement structures. Li (2009) concluded that the incorporation of up to 15% limestone fillers as a partial replacement for fine aggregate in low strength concrete or 10% limestone fines for in high strength concrete improved compressive strength. Another study on limestone as aggregate for concrete, Lian and Zunge (2010) found that the aggregates partial replacement to be feasible (as shown in Table 2.13). This finding is supported by Huang et al. (2010) in his study on laboratory evaluation of permeability and strength of polymer-modified pervious concrete.

Table 2.13: Compressive strength using different aggregates (Lian and Zunge 2010)

Curing time (days)	**Compressive strength (MPa)**						
	Quartzite		**Dolomite**			**Limestone**	
	A_1	**A_2**	**B_1**	**B_2**	**B_3**	**C_1**	**C_2**
7	11.6	13.0	15.0	16.0	14.3	14.3	13.5
28	11.8	15.5	15.8	19.0	15.5	15.5	14.0

2.22 Marble

Marble is a granular metamorphic rock derived from re-crystallized carbonate minerals, most commonly calcite, serpentine (hydrous magnesium iron phyllosilicate) and dolomite (Martin 2013). Basically, there are two ways of marble formation; (i) marble is formed from old limestone layers in the earth's crust subjected to high thermal stress due to the movement of the earth layer or (ii) marble is formed as the result of contact metamorphism near igneous intrusion (Bonewitz 2012). The major mineral in marble is calcite and the minor minerals that might contain in marble are diopside, tremolite, actinolite and dolomite (Polk 2012). Table 2.14 enlists the physical and chemical characteristics of marble (Sivakugan et al. 2013).

Table 2.14: Physical and chemical properties of marble (Sivakugan et al. 2013)

Physical Properties	
Hardness (Mohs)	3 to 4
Density (kg/m^3)	2.5 to 2.65
Compressive Strength (kg/cm^2)	1800 to 2100
Water Absorption (%)	< 1
Porosity	Quite low
Weather Impact	Resistant
Chemical Properties (%)	
Lime (CaO)	38 - 42
Silica (SiO_2)	20 - 25
Alumina (Al_2O_3)	2 - 4
Other Oxides like Na, Mg	1.5 to 2.5
Loss On Ignition (LOI)	30 - 32

2.22.1 Applications in Concrete and Mortars

The amount of the marble dust (MD) as a waste from the marble industry significantly increasing in the world (Ortiz et al. 2009). The utilization of the marble dust waste as filler in mortar and concrete has become a top priority. Topcu (2009) suggested marble dust as filler or substitution, materials effects the pores between the aggregates altering the impermeability of the concrete produced thus the durability of concrete. The identified crystalline phases of marble dust were calcite and dolomite. It contains CaO, SiO_2 and small amount of MgO, Al_2O_3 and Fe_2O_3 (Figure 2.37).

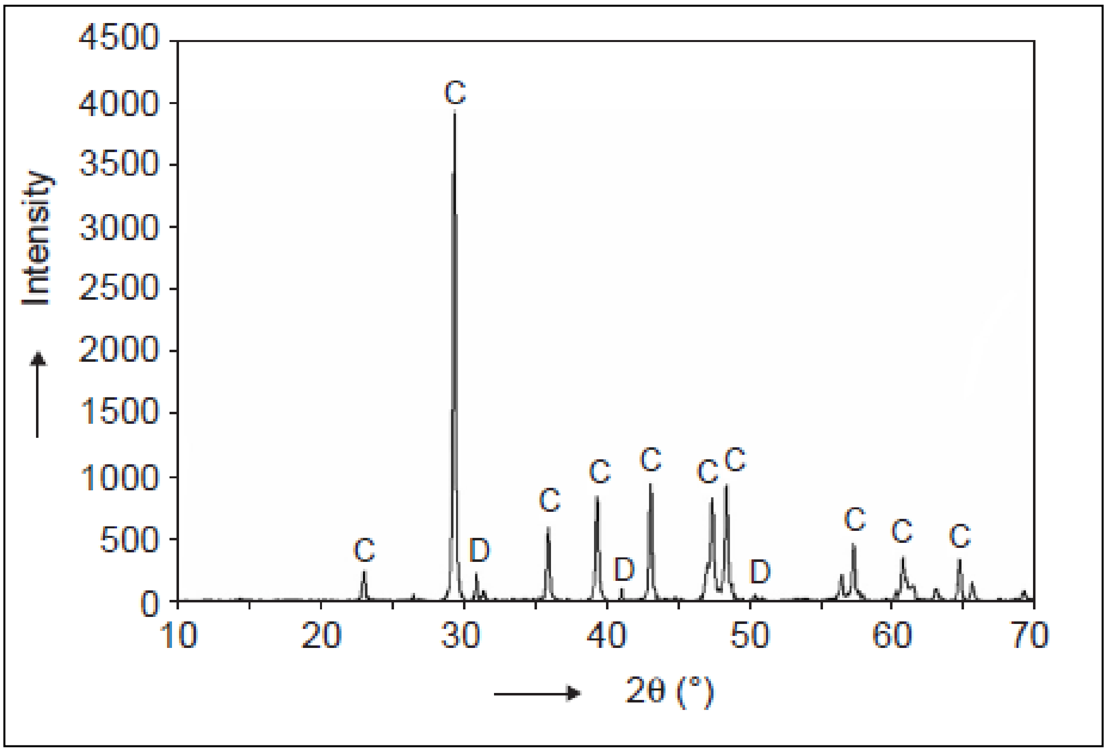


Figure 2.37: XRD spectrum of marble dust (Kavas and Olgun 2007)
Note: C: calcite, D: dolomite

It was observed that the use of marble dust as a filler does not affect the setting time although the fluctuation of compressive strength values occurred in between substitution percentages (Aruntaş et al. 2010). A recent study by Corinaldesi et al. (2010), in terms of mechanical performance indicating that 10% substitution of sand by the marble powder in the presence of a super plasticizing admixture provided a maximum compressive strength within the same workability level, that was comparable to that of the reference mixture after 28 days of curing. Binici et al. (2008) suggested the effects of marble aggregates on the compressive strength of concrete were strongly influenced by its marble content even though the values were intermediately compared to other materials. It was later can be concluded that marble waste aggregates can be used to improve the mechanical properties, workability and chemical resistance of the conventional concrete mixtures.

2.23 Precipitated Calcium Carbonate

Precipitated Calcium Carbonate (PCC) also known as purified or refined calcium carbonate is a synthetic calcium carbonate. It has the same chemical formula as the other types of calcium carbonates such as limestone, marble and chalk. Precipitated calcium carbonate synthetically processes from naturally occurring limestone or by dissolving limestone and precipitating calcium carbonate as very fine particles using carbon dioxide (Aroganite Process) or sodium carbonate (Solvay Process) (Dick and Annicelli 2001).

2.23.1 Precipitated Calcium Carbonate Applications

Precipitated calcium carbonate is widely used as sorbents to "capture" another substance. Calcium carbonate is used the process of capture and long-term storage (or sequestration) of atmospheric carbon dioxide (Tahija and Huang 2011, Ghosh-Dastidar et al. 1996, Veltman et al. 2010).

In a powdered form, calcite often has an extremely white colour. Powdered calcite is often used as a white pigment or "whiting" (Mills et al. 2008). Some of the earliest paints were made with calcite. It is a primary ingredient in whitewash and it is used as an inert colouring ingredient of paint. It does not only provide an economical advantage, but it also modifies some physical paint properties (Karakaş and Çelik 2012). Wu et al. (2006) successfully conducted a series of experiments using nano-calcium carbonate in the form of filler cake as a composite particles that have a great potential applications in painting.

2.23.2 Precipitated Calcium Carbonate as Filler

Precipitated calcium carbonate is a versatile additive for use in wide range plastic and elastomeric applications (NPCS 2012b). Its regular and controlled crystalline shape and ultra fine particle size together with the hydrophobic surface coating combine to the benefit of polymer processing and subsequent physical properties (NPCS 2012a).

Morphology of precipitated calcium carbonate gives different properties to end-product (see Figure 2.38). Plate-like calcium carbonate particles are desirable in paint making industry, which may confer high smoothness and excellent gloss to the paper sheet since they are easily aligned in a regular way and may confer high electric resistance and elasticity modulus to the composite (Wen et al. 2003). Prismatic shaped of precipitated calcium carbonate are designed to give high brightness and whiteness (Wise 1997).

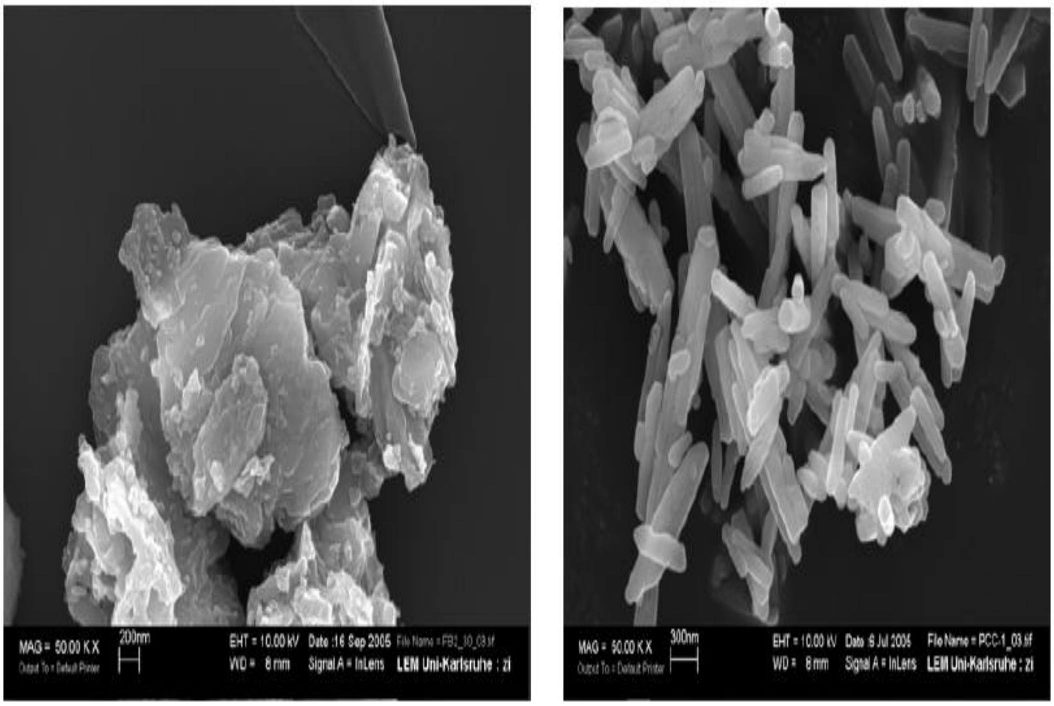


Figure 2.38: SEM images of PCC aggregates in plate shape (left) and prismatic shape (right) (Wise 1997)

2.23.3 Particle Size

Particle fineness is important for calcium carbonate effectiveness. It is hypothesized that chemical reaction effect is greater with small particles because of increased total surface area exposed to the mixture compounds. This is because calcium carbonate dissolves slowly, so its effectiveness is limited to a small area around each particle (Peters et al. 1996).

In Western agricultural, calcium carbonate is use to increase soil pH (correcting the soil acidity) (West and McBride 2005). The calcium carbonate fineness plays an important role in lime's effectiveness at neutralizing soil pH. This is due to a larger surface area increases the limes solubility rate. The effectiveness of lime aggregates at various particle sizes shown in Figure 2.39.

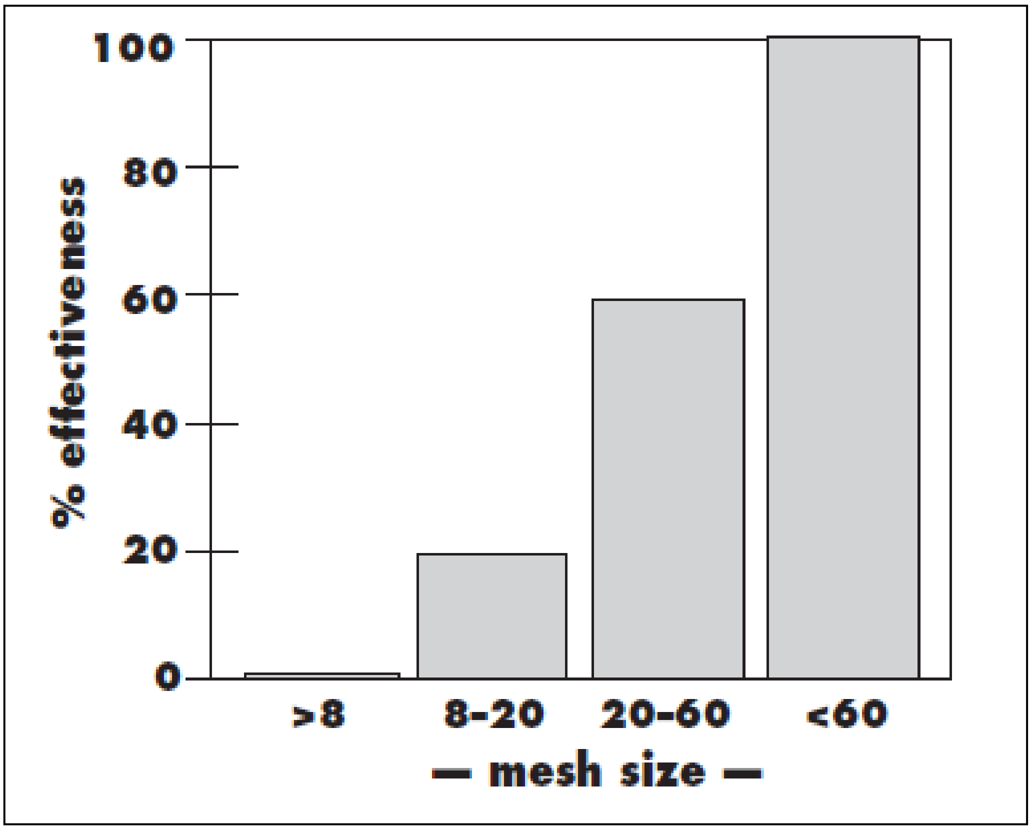


Figure 2.39: Effectiveness of $CaCO_3$ according to particle sizes (Peters et al. 1996)

2.24 Conclusions from the Literature Review

The previous research highlighted in this chapter illustrates the performance benefits of the utilisation of lime mortars as a traditional and environmental material for construction. The introduction of calcitic fillers in concretes and mortars have been shown to have both positive and negative performance characteristics in modified materials but most studies do not specifically relate to lime mortars.

Insufficient amount of literature has been published relating to the implications of lime mortar being cured in high temperature and humidity environments. This research is further diluted when attempts to evaluate the influence of seeding additives for the climatic conditions are assessed. Clearly, the research in this thesis was undertaken to identify if there is a positive influence of seeding formulations of natural hydraulic lime cured in unfavourable environmental conditions and to evaluate the physical and chemical characteristics.

Generally, the literature relating to calcitic additives focuses on substitution of aggregates and not specifically the influence upon the binder. The importance of the use of by-product seeding materials has been shown to potentially yield great environmental benefits.

Seeding with calcitic fillers may therefore yield significant environmental and economic benefits to enhance the use of lime mortars. It is believed that seeding may be applied to modify a mortars hydration kinetics and microstructure development. Furthermore, calcitic filler acts as the crystallization nucleus for the precipitation of lime binder hydration.

The next chapter establishes the research methodology and multi parameter experimental procedure. The study was subjected to different climatic conditions; (i) 20°C with 60% RH; (ii) 27°C with 90% RH and (iii) 33°C with 90% RH. The experiments will be divided into five major stages with seven experiments.

CHAPTER 3
METHODOLOGY

3.1 Introduction

The research programme has been designed in order to investigate the influence of calcium carbonate filler modification in natural hydraulic lime mortars in high temperature and humidity climatic conditions. Benachour et al. (2008), indicates that mortar performance and durability can be quantified as being related to two main properties, namely; micro structural and mechanical. Micro structural can be sub-divided into studies relating to amongst others; density, porosity, pore size distribution and capillary absorption, whilst mechanical include; Young's modulus, compressive and flexural strength. This work and its methods rely upon components from both these areas and have been carefully prepared, and organized with compatibility and reproducibility as an integral component. Additional work has been undertaken to evaluate the surface characteristics of the range of materials. The tests, wherever possible, conformed to British Standards in attempts to obviate or minimize error as shown in Figure 3.1.

3.1.1 Experimental Programme

The experimental programme was planned considering the following criteria;

a. mix ratios (volume, binder to aggregate proportions and water ratios);
b. mineral composition of aggregate adopted;
c. the particle size of calcite to be integrated.

These are critical factors in determining the strength development of natural hydraulic lime mortars and the influence of seeding reaction cured in different temperature and relative humidity conditions. Nine mortar formulations with varying calcitic aggregate seeding materials were manufactured from two principal bases. 21 specimens were manufactured for each formulation (see Table 3.1). Preliminary experiments were carried out upon unadulterated samples to act as a performance datum.

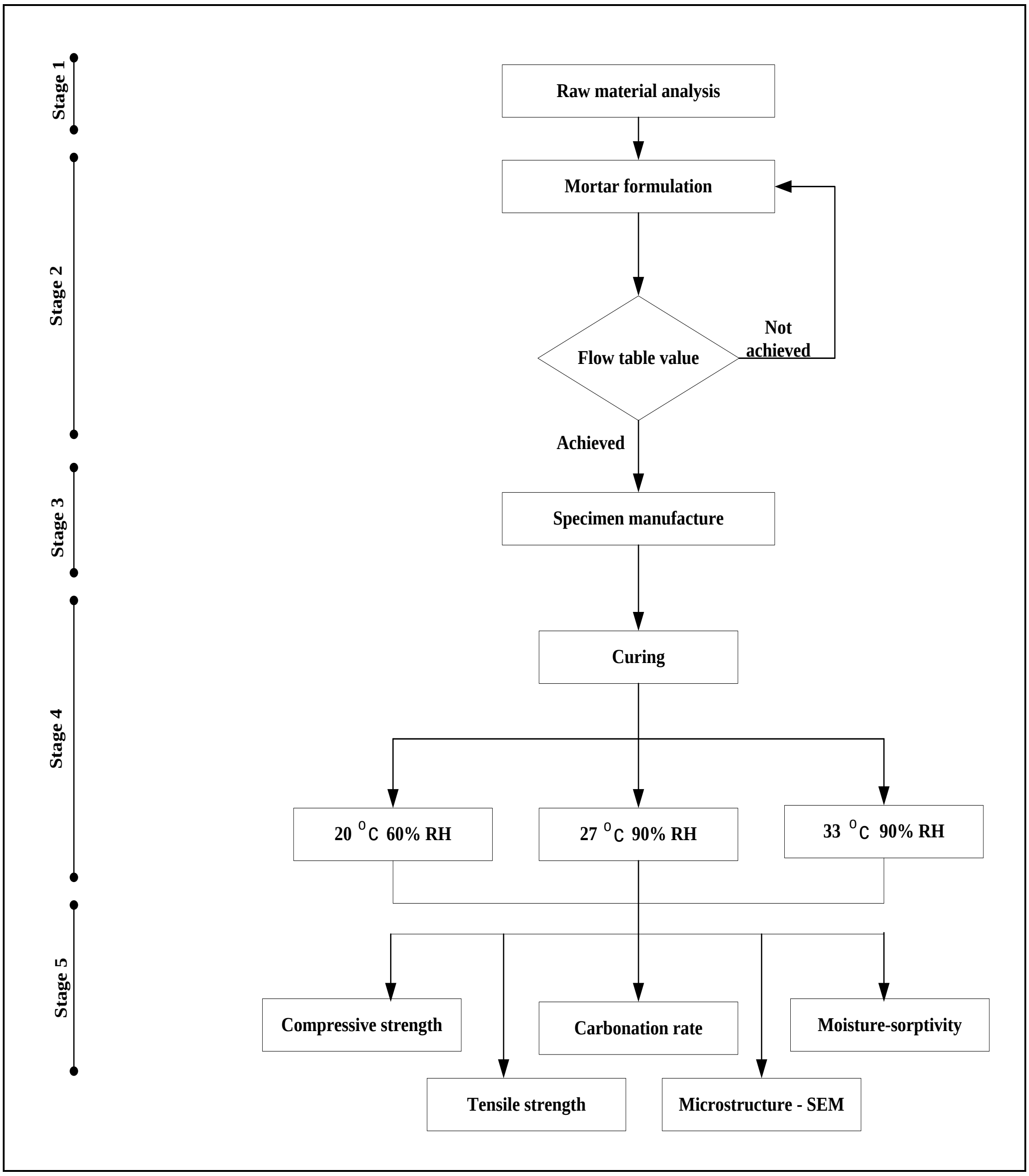


Figure 3.1: Research Methodology Schematic Diagram

The mortars were subjected to different climatic conditions; such as temperature and relative humidity (RH). Climatic simulations were carried out under constant conditions for three types of weather; (i) 20°C with 60% RH; (ii) 27°C with 90% RH and (iii) 33°C with 90% RH. These conditions reflect the average high temperature and humidity encountered in Malaysia and the wider geographical region. All specimens were placed in the TAS Environmental Curing Cabinet under the aforementioned conditions. To ensure satisfactory carbonation, a carbon dioxide (CO_2) injection system was designed and installed, enabling a constant CO_2 level to be maintained.

Table 3.1: Experimental Programme

Specimen Code	Seeding Formulation		Curing Conditions		
	Material	Amount			
1 (Control)	-	-	20°C, 60% RH	27°C, 90% RH	33°C, 90% RH
2	Oyster shell	6%			
3	Oyster shell	10%			
4	Limestone	6%			
5	Limestone	10%			
6	Marble	6%			
7	Marble	10%			
8	Precipitated $CaCO_3$	6%			
9	Precipitated $CaCO_3$	10%			

It was suggested by Skoulikidis et al. (1995) and Skoulikidis et al. (1996) that 6% of seeding is sufficient to increase the carbonation rate and mechanical resistance of newly seeded mortar. Therefore, the seeding amount of 6% was chosen for this research. There is no literature specifically relating to about the maximum amount of calcite that can be used to effectively modify the materials. 10% was chosen for comparison purposes.

3.2 Stage 1: Raw Materials Analysis

Control samples were manufactured using a St Astier NHL 3.5 (moderately hydraulic) lime binder and a well graded coarse sand. These materials were selected on the basis of being commonly used for the repair of the traditional built environment and being relatively representative of historic mortars. Material characterisation was based on sieve analysis of the aggregate in accordance with BS EN 13139 (2002), to determine the grading profile. Powder X-Ray diffraction (XRD) was also utilised to determine the mineralogy.

3.2.1 Binder

St Astier was selected for the sample manufacture as it is one of the most commonly used binders in the United Kingdom and is therefore considered as being reflective of site practice. The lime used in this research was commercially available St Astier NHL 3.5 (moderately hydraulic). It is manufactured from ancient marine sediment in Dordogne, France. This product was chosen due to its high percentage of available lime and conformity with EN 459-1: 2010 and it contains no tri-calcium aluminate (C_3A). Gypsum ($CaSO_4$) and insignificant traces of minor elemental anhydrous mineral compounds were present. NHL 3.5 (moderately hydraulic) was used for the control samples prior to the addition of seeding materials. The anhydrous NHL3.5 binder composition was established through technical data provided by the manufacturer (shown in Table 3.2).

Table 3.2: Physical and Chemical Data of St. Astier NHL 3.5

Physical Characteristics	NHL 3.5
Combined silica bands	8 - 12
Available lime (%)	20 - 25 (> 9)
Density (gr/litre)	600/660 (500-900)
Surface cover (cm^2 per gram)	9000
Granulometry: Residue @ 0.09 mm	6.5%
Whiteness Index (Y)	72
Compressive strength N/mm^2 (based on 28 days)	3.5 - 8
Flexural strength N/mm^2 (based on 28 days)	2
Soundness (max. 2mm)	< 1mm
Set, beginning (1-15 hours)	5 - 6
Chemical Composition	**Amount (%)**
Ignition	18
Calcimetry (CaO_2)	11
Insoluble	9.6
Calcium Oxide (CaO)	56
Silicon Oxide (SiO_2)	12
Aluminum Oxide (Al_2O_3)	1.66
Iron (III) Oxide (Fe_2O_3)	0.49
Sulfur Trioxide (SO_3)	0.45
Magnesium Oxide (MgO)	0.98
Manganese(II) Oxide (MnO)	0.01
Titanium Dioxide (TiO_2)	0.16
Potassium Oxide (K_2O)	0.16
Sodium Oxide (Na_2O)	0.06

3.2.2 Aggregates

Well graded silica sand from Cloddach, Perthshire (Figure 3.2) was selected as it is representative of materials commonly used for the repair of traditional masonry structures in Scotland. Silica sands contain a high proportion of silica (more than 95% silica oxide, SiO_2). Silica sands are valued for a combination of chemical and physical properties. These include high silica content in a form of quartz. Silica sands usually have a very low level of damaging impurities; in particularly clay, iron oxide and refractory minerals (Bloodworth et al. 2009). Silica sands have typically a narrow-grain size distribution of 0.5 to 1.0 mm range. Figure 3.2 shows SEM image of silica sand.

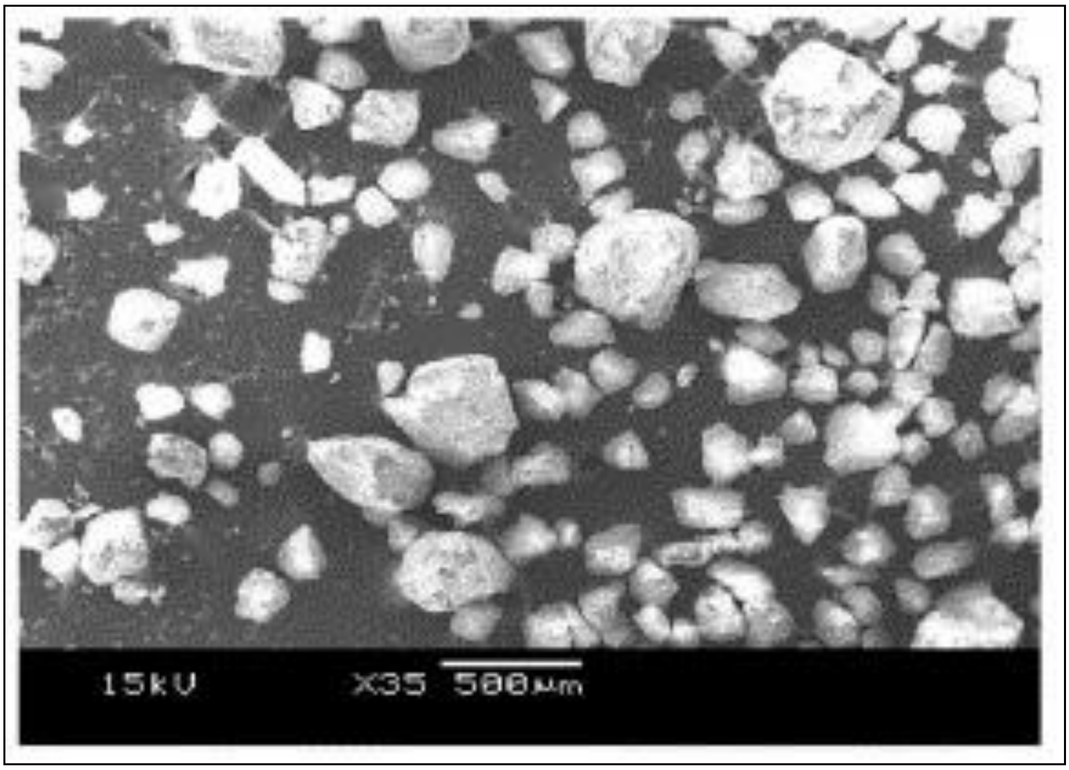


Figure 3.2: SEM image of silica sand (Tang et al. 2003)

This aggregate ensured isolation of variables due to an absence of calcitic mineral components. The grading curve was ascertained in accordance with BS EN 13139 (2002). The bulk density of the aggregate was determined to be 1630 grams/litre.

3.2.3 Sand Grain Size Distribution

In order to establish the grain size distribution, dry sieve method following BS EN 933-1:2012 was applied to separate the sand grain according to the different size fractions and proportions (Leslie and Gibbons 2005). The silica sand had been cleaned and allowed to dry in an oven (to eliminate water) at 105-110 °C for 24 hours prior to the sieving process. 1000g of sand was assessed passing through sieve mesh sizes; 4.000 mm, 2.360 mm, 1.000 mm, 0.500 mm, 0.25 mm, 0.125 mm and 0.063. The fraction retained on each sieve was weighed to the nearest ± 0.05g and expressed in cumulative percentage passing as shown in Figure 3.3.

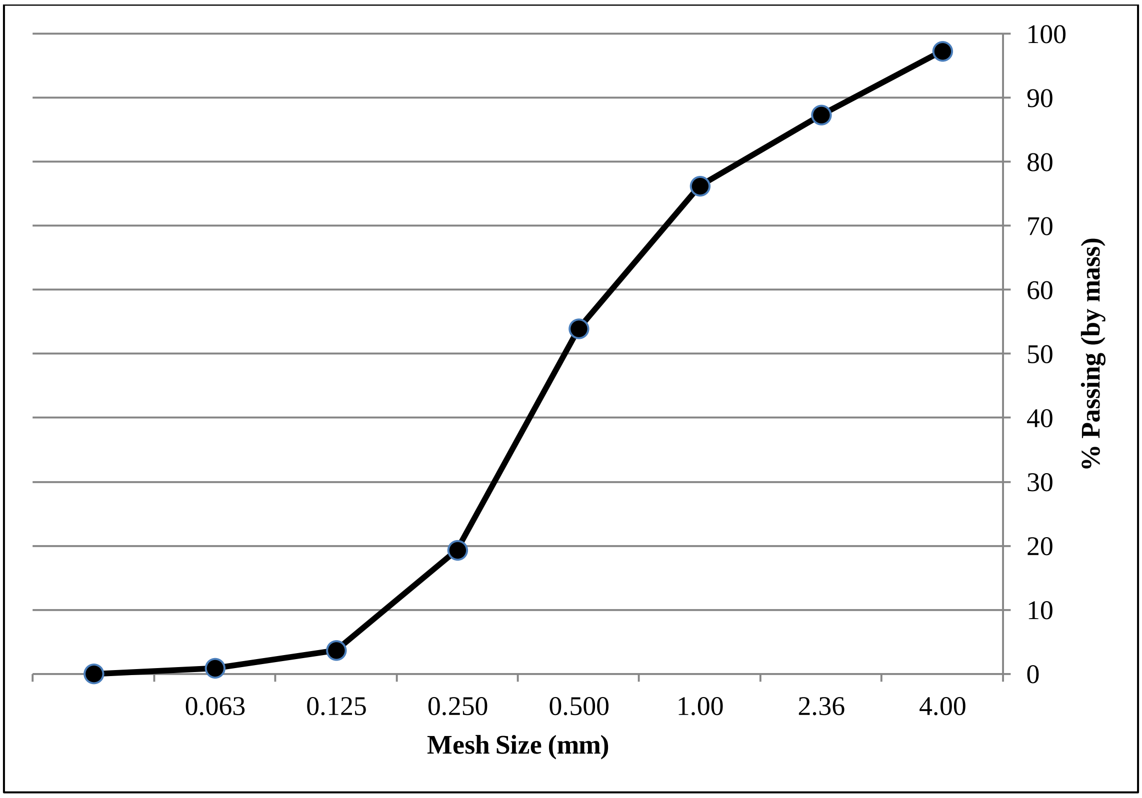


Figure 3.3: Grain size distribution of sand aggregates

3.2.4 Seeding Materials

Four types of calcite were procured for use as seeding materials, namely; (i) precipitated calcium carbonate ($CaCO_3$) (ii) oyster shells, (iii) limestone chippings and (iv) marble as shown in Figure 3.4. All the calcitic seeding materials were mechanically crushed, using Denison Universal Test Machine (Model T.42.B.4) and sieved to attain a particle size in the range of 250-300μm.

Oyster shells: The selected oyster shells were composed of approximately 98% of $CaCO_3$ and other trace minerals being present (Yoon *et al*. 2003). Oyster shells are common waste materials found in coastal region of South-east Asia and are therefore realistic substitute materials for study. Three polymorphs of calcium carbonate i.e. aragonite, calcite, vaterite are associated with the bi-valve shell (Poigner *et al*. 2011). The exact polymorph would vary based on several factors such as the species, molecular impurities in the shell and the number and frequency of proteins embedded in the shell (Cocks 2009).

The oyster shells originated from Northern Ireland. The shells were physically and chemically treated beforehand. The processing includes washing, crushing, drying and heating, thus ensuring the product is free of salmonella. It is also tested by the supplier for dioxin and heavy metals, and shown to be microbiologically free of pathogenic micro-organisms and mycotoxins.

Limestone chips: The limestone chips are sedimentary rocks. They are composed largely of $CaCO_3$ calcite and aragonite polymorphs minerals. The limestones used in this study were light grey limestone derived from Bankfield Quarry, Lancashire, United Kingdom (Grid reference: 755 745) and were initially procured as 10mm chips prior to crushing.

Marble chips: The angular shaped Turkish Arctic White marble (3-8 mm) was used. This pure white marble is the result of metamorphism of a very pure (silicate-poor) limestone or dolomite protolith.

Precipitated calcium carbonate (PCC): Precipitated calcium carbonate (98% pure) with particle size distribution of 100 mesh was used as point of reference to ensure consistency (composition of Carbon= 12%; Calcium= 40.04% and Oxygen= 47.96%). The precipitated calcium carbonate was supplied by Fisher Scientific in 3kg container. It has a Formula Weight (FW) of 100.09. The specification of the material was provided by the supplier as follows;

Table 3.3: Precipitated calcium carbonate specification sheet

Test	Guaranteed	Units
Assay	≥ 98	%
Copper (Cu)	≤ 100	ppm
Iron (Fe)	≤ 200	ppm
Lead (Pb)	≤ 10	ppm
Magnesium (Mg)	≤ 2000	ppm
Potassium (K)	≤ 500	ppm
Sodium (Na)	≤ 2000	ppm
Total chloride (Cl)	≤ 0.05	%
Total phosphorus (P)	≤ 500	ppm
Total silicon (Si)	≤ 1000	ppm
Total sulfur (S)	≤ 500	ppm
Zinc (Zn)	≤ 100	ppm

Figure 3.4: Calcitic materials (before crushing process). (a) Oyster shells (b) Limestone chips (c) Marble chips and (d) Precipitated $CaCO_3$

3.2.5 Calcitic Materials Analysis

XRD samples were analysed on a Thermo ARL X'TRA Diffractometer with a 2 Theta range of 5° - 70° at a rate of 1°/min to determine mineral composition of the calcitic seeding materials. The XRD spectra are shown in Figure 3.5, 3.6, 3.7 and 3.8. Both the crushed limestone and precipitated calcium carbonate are purely calcite. The oyster shells consist of both calcite and aragonite. The crushed marble appears to be a mixture of calcite and dolomite (calcium magnesium carbonate). The use of XRD would have permitted the analysis of the proportions of dolomite and calcite to be determined. However, due to time and resource constraint, the analysis cannot be accomplished.

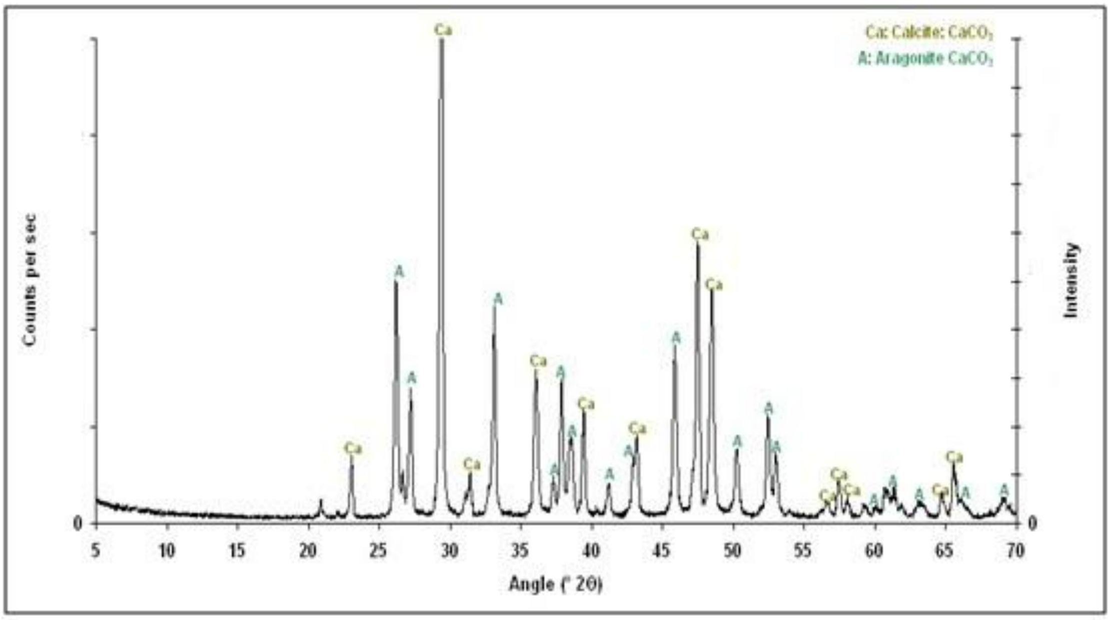


Figure 3.5: XRD analysis of oyster shells

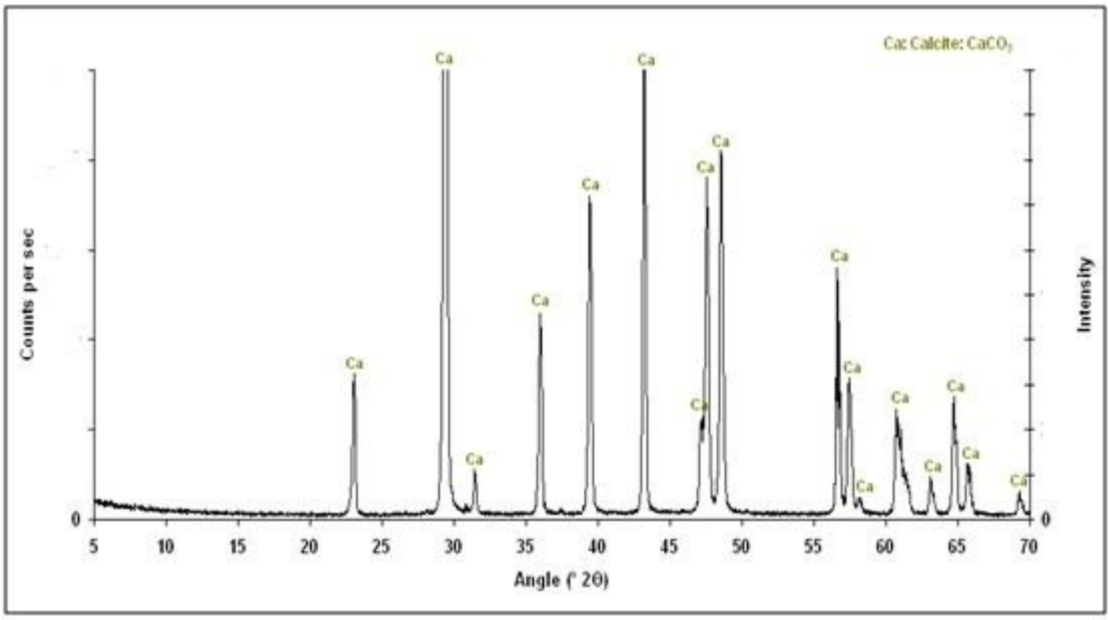


Figure 3.6: XRD analysis of limestone

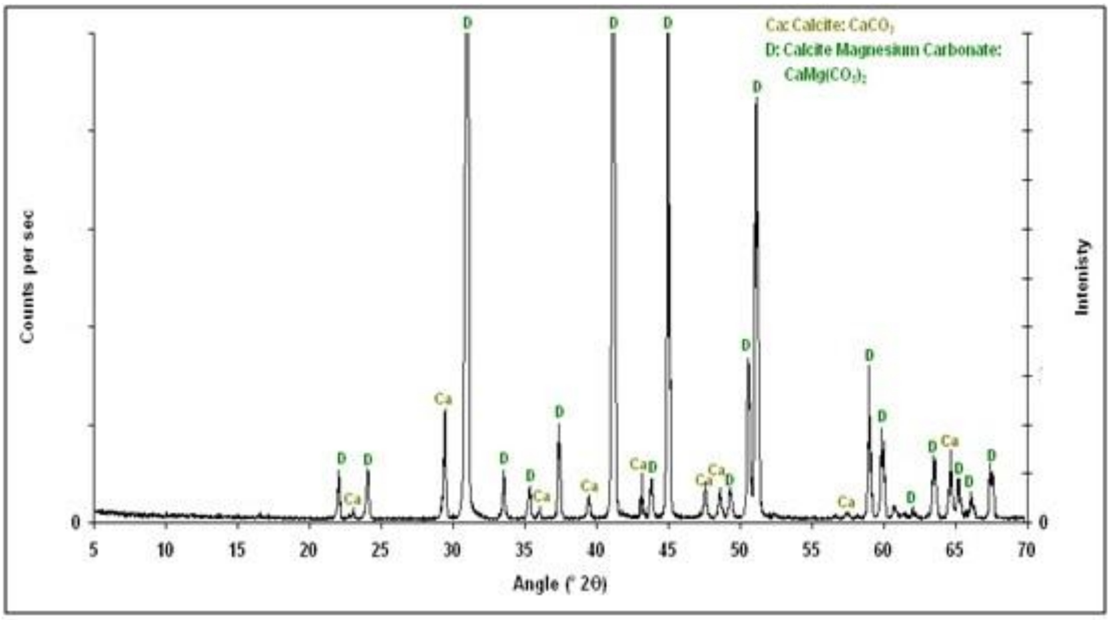


Figure 3.7: XRD analysis of marble

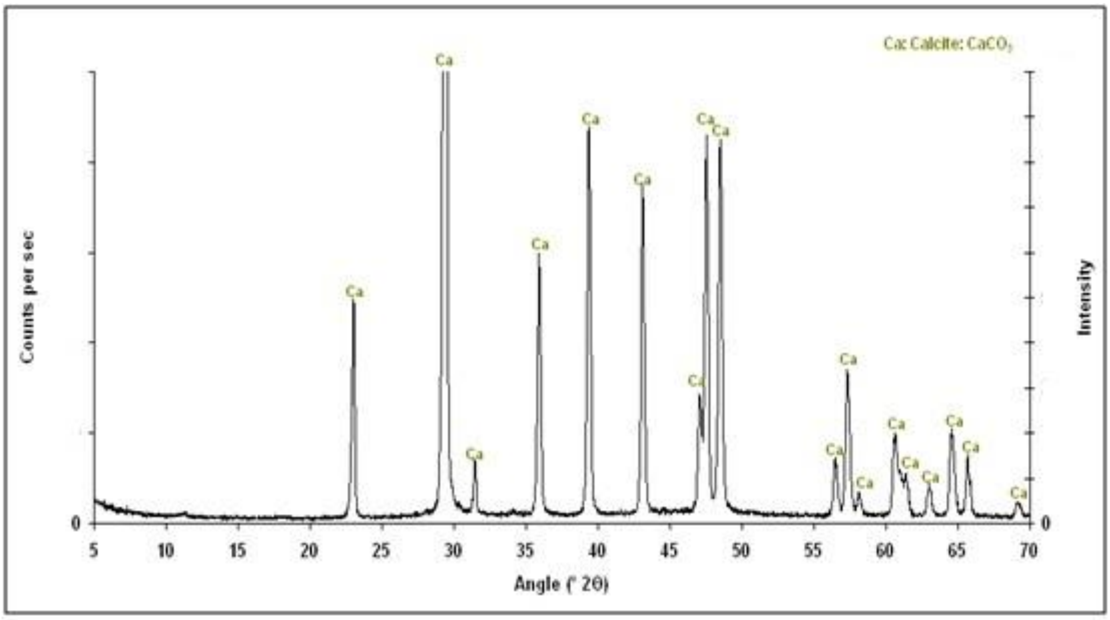


Figure 3.8: XRD analysis of precipitated calcium carbonate

3.2.6 Water

Distilled water was used to ensure that salts and other impurities were removed from the water. This was necessary to achieve control of variables and ensure precise results in any testing. Distilled water is important to maintain the integrity of the mortar properties. The water volumes (mL) were converted to weight unit (g) to avoid measurement imprecision during mixing process.

3.3 Stage 2: Mortar Formulation (Initial determination)

The mortars rheological properties were obtained using the amount of water required to achieve normal consistency and good workability (measured by the flow table test). The water content was ascertained using a hand operated slump / flow table apparatus conforming to BS EN 459-2:2010. In order to determine the flow diameter, the mortar was filled uniformly into the flow table mould and then lightly tamped ten times with the tamping rod. The mould was slowly removed from the plate and the mortar was subject to the standard jolting procedure. This was undertaken 15 times. The spread diameter then was measured using the digital caliper with ± 1mm error (see Figure 3.9). The consistency was determined by flow table and was found to be 165 mm ± 2mm.

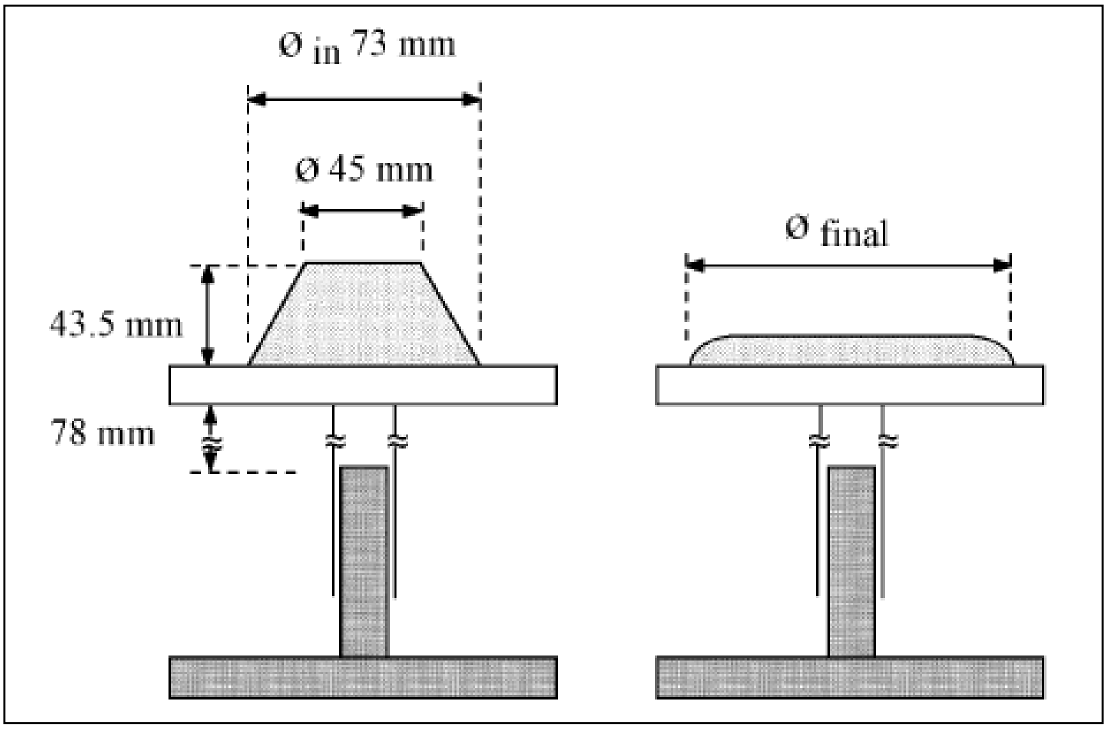


Figure 3.9: Schematic diagram of flow table test (Nadif et al. 2002)

For NHL 3.5, the standard required flow diameter was to be 165 ± 3 mm. If the required flow diameter was not achieved with the selected amount of water, a correction process was undertaken. This enabled the determination of the correct amount of water specifically modified for variation in compositional change. The result of this was the drawing of a graph correlating the flow diameter with the quantity of water. This was essential for reproducible accuracy of water content. Figure 3.10 shows the flow table test results on the mortar mixes (the water content was weighted to the nearest 1g). Table 3.4 indicates the quantities of constituents required for the preparation of 1 litre of mortar. The same amount of water was used for mixing the modified mortars. This was intended for consistency.

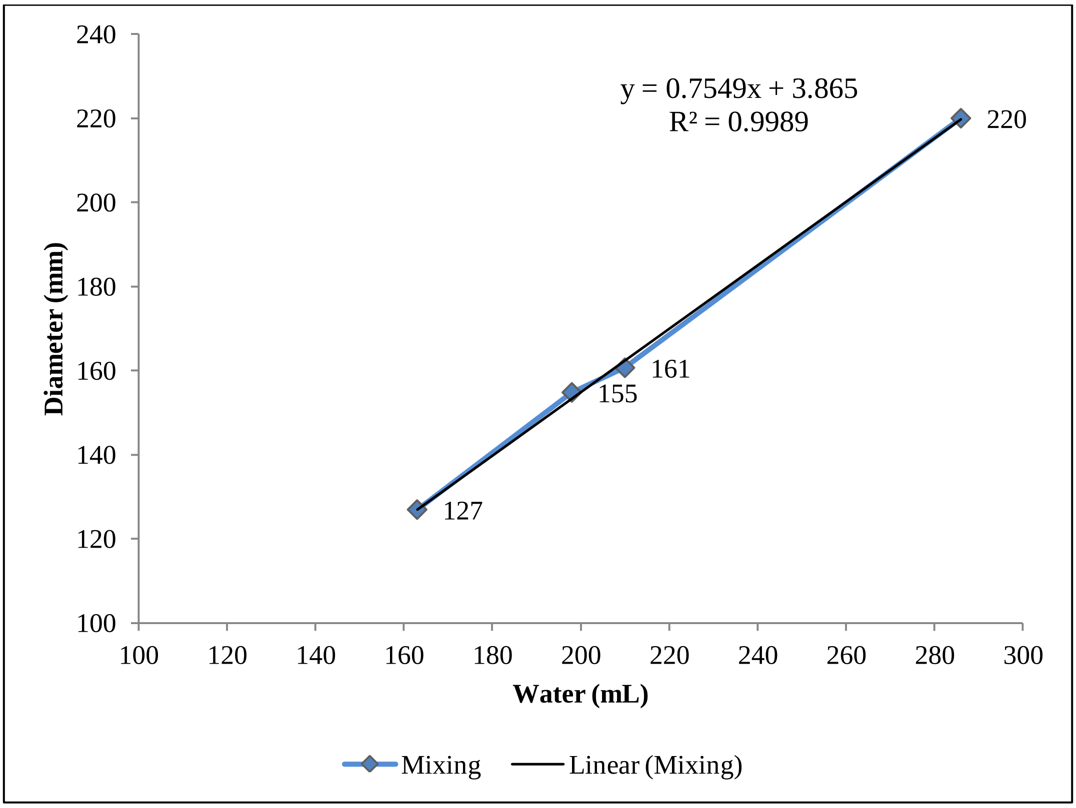


Figure 3.10: Flow table results

Table 3.4: Mortar manufactures constituents and flow value

NHL designation & Relative Bulk Density (RBD) (g/L)	Constituent amounts of materials in mortar used in slump test			Flow value (mm ± 2mm)
	Mass of NHL (g)	Mass of sand (g)	Mass of water (g)	
650	207.9	1564.0	332.0	165

3.4 Stage 3: Specimen Manufacture

Samples were prepared using a binder/aggregate ratio of 1:3 by volume. The mix proportions were selected based on the void ratio of the aggregate, and the requirement of the lime binder to fill the voids between aggregate grains to produce a ‘complete’ mortar. Cloddach sand has a void ratio of approximately 33%, hence the ratio of one part binder to three parts aggregate. All materials were batched by weight (in grams) to ensure accuracy.

3.4.1 *Mixing*

The manufacturing regime in BS 459-2 (2010) was modified to integrate the relative bulk density (RBD) calculations for the NHL 3.5 binder, resulting in an alteration of the quantity of binder from the standard 450g established in BS EN 196-1 (1999) to 189g. This adjustment was undertaken to ensure the 1:3 ratio was maintained for the manufactured samples.

The mortar was prepared by the ‘dry mixing’ method undertaken by various authors (Allen et al. 2003, Ball et al. 2009). The samples were batched adopting the proportions as shown in Table 3.6, and mixed mechanically for 4 minutes in a bench top paddle mixer (Crypto Peerless Model 220/250) at low speed. The sides of the mixer bowl were scraped after 2 minutes to ensure all the dry powder was incorporated into the mix. Water was added and mixed for 5 min at low speed, and finally for 1 min at high speed.

3.4.2 *Polystyrene 3-Gang Moulds*

Mixing and casting of mortars was undertaken in accordance with BS 459-2 (2010); with the exception that the 160 x 40 x 40 mm steel 3 gang moulds being substituted for 160 x 40 x 40 mm single use polystyrene 3-gang moulds as shown in Figure 3.11.

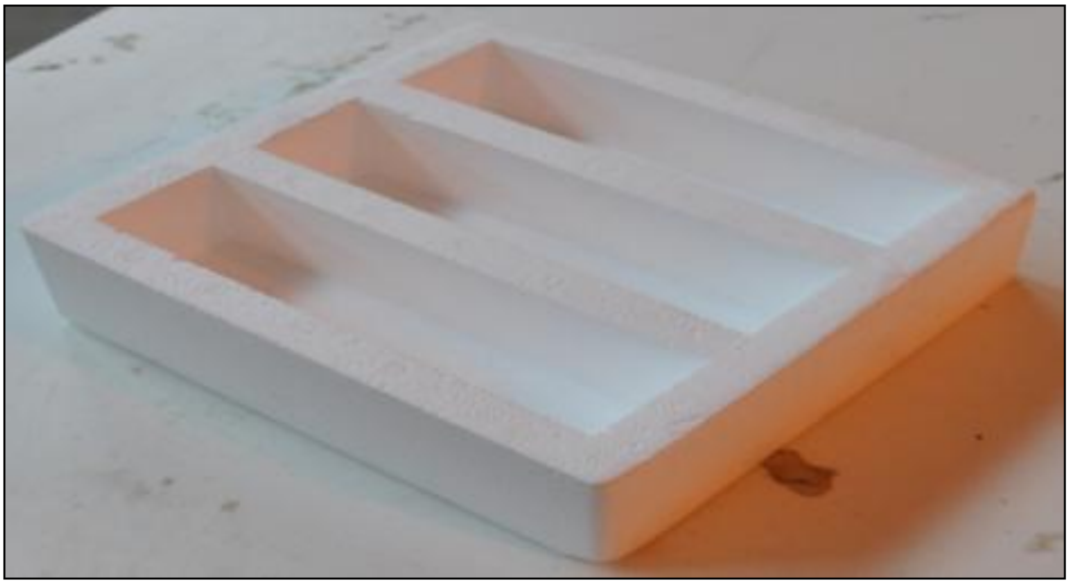


Figure 3.11: 160 x 40 x 40 mm single use polystyrene 3-gang mould

Polystyrene moulds offer several benefits; ease of use; reduced weight in the environmental curing cabinet; and the elimination of the need for releasing agent which may pose uncertainties regarding the interaction of the two surfaces and may compromise the evaluation of seeding materials. Upon casting into moulds, an automatic vibrating table (50Hz with a level of 18.5 ms^{-2} RMS acceleration) was used to compact mortar samples, removing any trapped air (BS 459-2: 2010).

Substituting the steel moulds with polystyrene moulds established a significant advantage in term of reducing the number of samples that were broken during de-moulding.

3.4.3 Mixing Formulations

The mortar mixes consisted of binder, aggregate, water and calcitic fillers. To ensure homogeneity and consistency, mixing formulations were undertaken based on relative bulk density (Table 3.5). This calculation was used to eliminate any inaccuracy in the amount of substitution materials required.

Table 3.5: Relative bulk density of the aggregates

Material	Density (kg/m^3)
Cloddach sand	1630
Oyster shells	1527.05
Limestone	1350
Marble	1625
Precipitated calcium carbonate ($CaCO_3$)	700

The aggregate (Cloddach sands) was weighed according to the mixing requirement. Aggregates in 250-300µm range were isolated via sieve analysis (shaken for 10 min). A total of 6% by weight of aggregates in that range were removed. The remaining 250-300µm range aggregates were mixed back into the container with sand from the sieve. Afterward, calcitic materials (oyster shells, limestone, marble and precipitated calcium carbonate) equaling 6% by volume of the aggregates were added to substitute the aggregates that were previously removed. The new modified aggregate combinations were then mixed with lime binder and water. These steps were repeated with 10% of the amount of aggregates removal. The overarching proportions of the lime mortars and relative quantities of substituted calcitic filler and water can be seen in Table 3.6.

Table 3.6: Mixing formulations*

Calcitic Filler	Sand (g)	Seeding (%)	Omitted Sand (g)	Omitted Sand Volume (L)	New Sand Weight (g)	Lime Binder (g)	Water (g)	Calcitic Filler Density (g/L)	Calcitic Filler Volume (L)	Calcitic Filler Weight (g)
Control	7200	0	0	0.00	7200	957.055	1528.53	-	-	-
Oyster shells	7200	6	432	0.27	6768	957.055	1528.53	1527.05	0.27	404.72
Oyster shells	7200	10	720	0.44	6480	957.055	1528.53	1527.05	0.44	674.53
Limestone	7200	6	432	0.27	6768	957.055	1528.53	1350	0.27	357.79
Limestone	7200	10	720	0.44	6480	957.055	1528.53	1350	0.44	596.32
Marble	7200	6	432	0.27	6768	957.055	1528.53	1625	0.27	357.79
Marble	7200	10	720	0.44	6480	957.055	1528.53	1625	0.44	596.32
Precipitated $CaCO_3$	7200	6	432	0.27	6768	957.055	1528.53	700	0.27	185.52
Precipitated $CaCO_3$	7200	10	720	0.44	6480	957.055	1528.53	700	0.44	309.20

*(*based on 7200g of sand)*

3.4.4 *Curing Chamber*

All specimens were placed in the TAS Environmental Curing Cabinet (Figure 3.12 and 3.13) under controlled environment as stated in the experiment programme (see Table 3.1). The samples were de-moulded 7 days after they were placed within the cabinet. Wet hessian cloth was used to cover the samples to prevent rapid moisture loss in the early stages of the setting of mortars.

To ensure satisfactory carbonation, a CO_2 injection system was designed and installed, enabling a constant CO_2 level at 450-500 parts per million (ppm). The CO_2 concentration readings were taken every morning throughout the curing period by using Portable CO_2 Meter (pSense Model AZ-0001).

Figure 3.12: TAS Environmental Curing Cabinet

Figure 3.13: View inside of the TAS Environmental Curing Cabinet

3.4.5 Specimen De-moulding

The specimens were de-moulded after 7 days with the polystyrene moulds being carefully cut using hand saw. The samples were eased out and placed onto a wire shelf for further curing. The weight of all specimens' were recorded and examined for any cracks or defect at this stage.

Figure 3.14: Shrinkage cracks in mortar specimens of 20°C - 60%RH

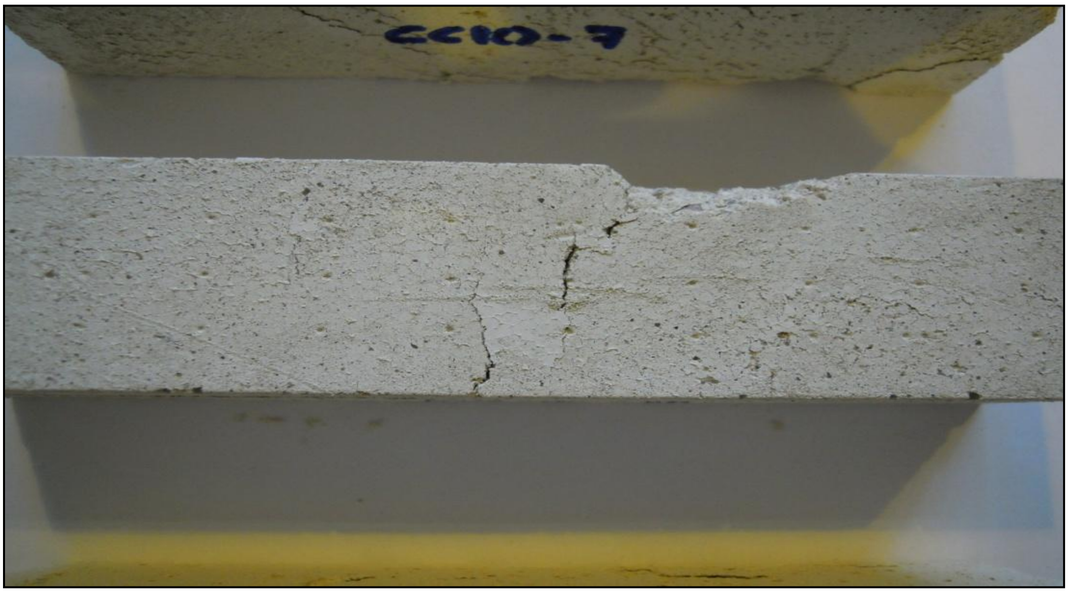


Figure 3.15: Shrinkage cracks in mortar specimens of 27°C - 90%RH

It was found that a large proportion of the specimens suffered from shrinkage cracks. This was especially pronounced for the limestone chips during 20°C - 60% RH (Figure 3.14). 20% of total of 27°C - 90% RH specimens suffered transverse crack in each specimen near the middle (Figure 3.15). In mortars cured under 33°C - 90% RH, the cracks were less frequent (Figure 3.16).

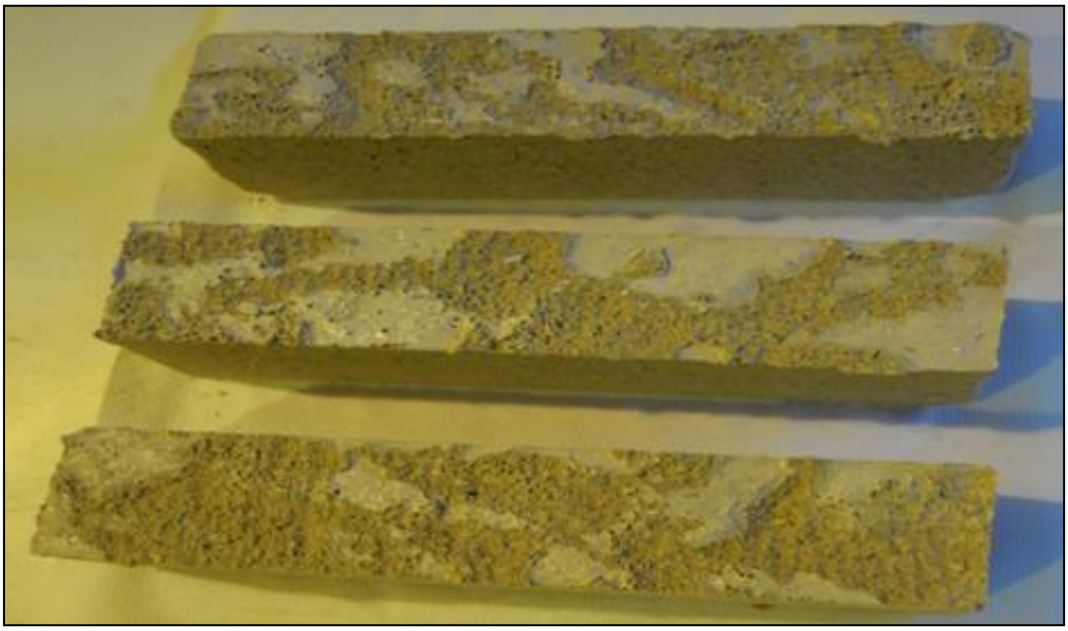


Figure 3.16: Shrinkage cracks in mortar specimens of 33°C - 90%RH

Due to this there were insufficient numbers of intact specimens to allow for three flexural tests to be conducted on each type of mortar. Whilst this undoubtedly allowed many of the 27°C - 90% RH mortar specimens to retain their integrity, it could not accommodate the higher shrinkage and cracking associated with the temperature and humidity. Additional shrinkage associated with the calcitic modifications cannot be discounted. A reduced amount of flexural strength data was however balanced by the additional data gained on the shrinkage data, compression strength test and carbonation profile. The time constrained experimental programme did not allow sufficient flexibility to remake replacement specimens.

3.5 Stage 4: Curing - Testing Duration

Climatic simulations were carried out under constant conditions for three types of climates; (i) 20°C with 60% relative humidity (RH); (ii) 27°C with 90% RH and (iii) 33°C with 90% RH matching the average climate of most hot and humid regions. The tests were performed at 7, 14, 21, 28 and 56 days respectively. Previous researchers used 365 days as a primary test date but this was deemed overly long for this work and a final test duration date of 56 days was adopted as a suitable alternative as suggested by Hanley and Pavia (2008).

3.6 Stage 5(a): Chemical Characterisation Testing

3.6.1 pH Value

The pH freshly cast mortars will be approximately 12 to 13 due to a high calcium hydroxide concentration, which is a normally associated with lime mortar prior to carbonation. As the mortar surface reacts with carbon dioxide in air, the pH of the surface gradually reduces to approximately 8.5 through the carbonation process.

The pH value was used to determine the changes during the hydration process. A Fisherbrand™ Plastic pH Strips (Figure 3.17) was used to measure the mortar pH. For fresh mortar, the pH strips were dipped into the mixture and the resulting colour was matched with the pH chart.

For hardened mortar (7 days and above), the method applied by Rasanen (2004) was used. The mortar samples used for the pH measurements were manually cut at the distance of 20 mm from the surface to avoid errors in measurements due to carbonation and moisture content gradient. The specimens then were crushed into a powder in a crushing press. After crushing, 15g of powder were mixed with 15g of distilled water.

Figure 3.17: pH strips

This test was repeated up to 5 times to ensure consistency and validity avoiding discrepancies between colour change determination.

3.6.2 Moisture Loss

After a mortar is placed it begins to dry as the moisture is liberated via evaporation. It is important to monitor the amount of water evaporated during the curing process to avoid less desirable effects like cracking and shrinking (Bentz et al. 2001).

The principle of free water as BS EN 459-2 has been used to form the basis of the process. Fresh mixed mortar was weighed (by using Mettler PC440 scale) to the nearest 0.001 g and stated as m1. After 7 days, the same mortar was then reweighed (to the nearest 0.001 g) and the reading was taken as m2. The value of water loss was then calculated as a percentage value as follows;

$$\text{Water Loss (\%)} = \left[\frac{(m_1 - m_2)}{m_1}\right] x\ 100\%$$

(Equation 3.1)

3.6.3 Carbonation Depth

The need to physically measure the extent of carbonation was achieved by spraying the freshly exposed surface of the mortar with a 1% phenolphthalein solution (Lo and Lee 2002). The freshly broken specimens were used to check the carbonation depth. The solution is a colourless acid/base indicator, which turns pink when the pH is above 9, denoting the presence of $Ca(OH)_2$ (shown in Figure 3.18). It indicates the boundary at which the carbonated front meets the un-carbonated mortar (where mortar is alkaline). The $Ca(OH)_2$ will turn pink while the carbonated portion is uncoloured. The depth of carbonation can then be measured. The phenolphthalein test is a simple and cheap method of determining the depth of carbonation in mortar.

Figure 3.18: Carbonation Depth Test

The depth of carbonation was investigated upon each mortar sample. This reflected the broad testing time intervals (7, 14, 21, 28 and 56 days). The samples were sprayed with phenolphthalein and the resulting stained material was recorded using a digital single-lens reflex camera (Nikon D90). The carbonation depth was measured by digital calliper (to the nearest 0.01 mm).

The upper side of the sample (which was exposed during curing) was labelled as side A and the side designation was labelled in a clockwise direction as shown in Figure 3.19. Each test was carried out based on repeating the process three times to ensure consistency. The average value was taken for the purpose of the calculation and graph plotting.

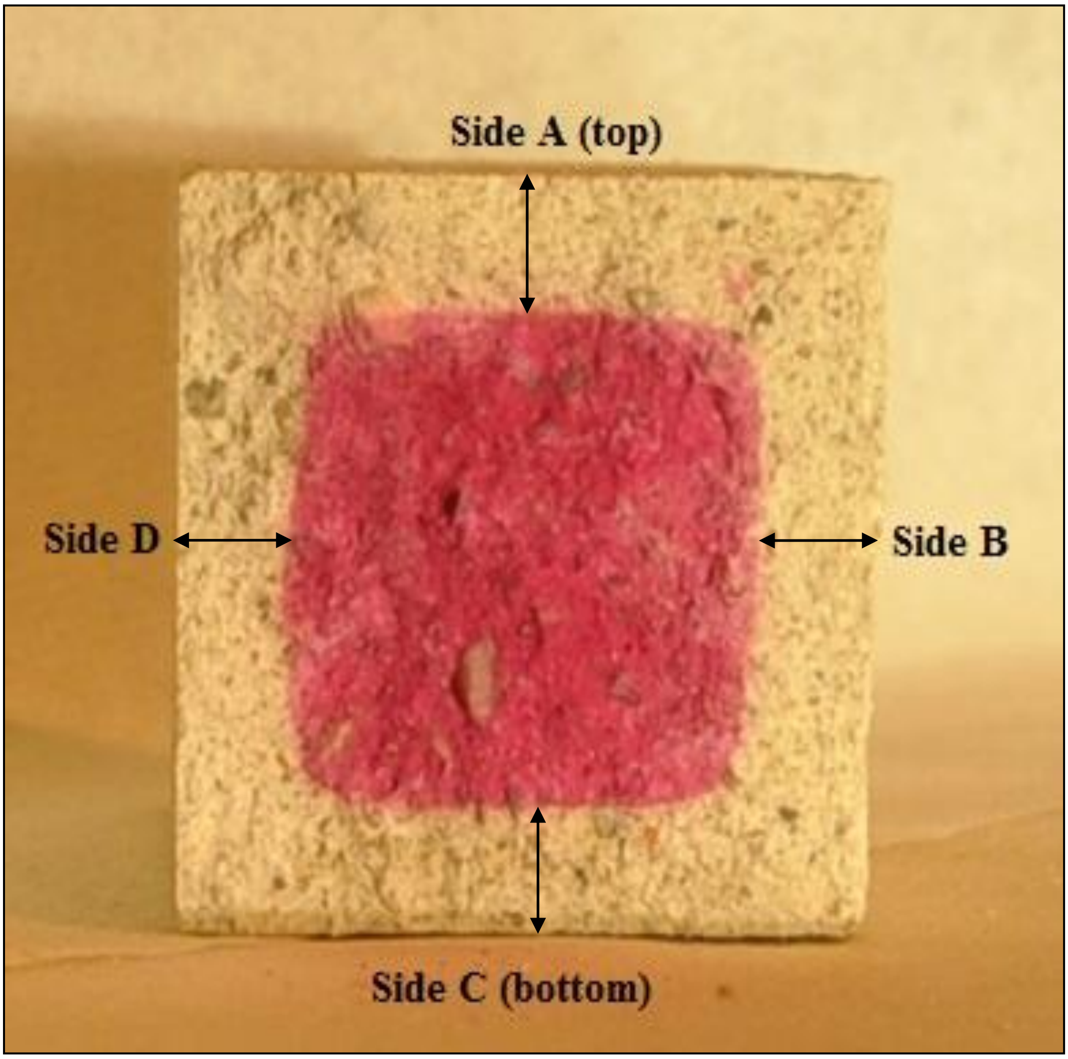


Figure 3.19: Carbonation depth measurement labelling

3.7 Stage 5(b): Physical Characterisation Testing

Testing was undertaken based on two principles; (i) to evaluate conformity with a specification or standard and (ii) to control or monitor the consistency of a product or process (Gray et al. 2010). For this research, flexural and compressive testing conforms to BS EN 459-2:2010.

3.7.1 Flexural Strength

The samples were tested for flexural strength (flexural response) using Lloyd's Universal Testing Machine (Model M5K) as shown in Figure 3.20. The three point flexural tests were carried out at low rates of loading (2 mm/min). The flexural testing apparatus used applied pressure to the sample until failure was detected. The machine continued to exert pressure until the sample broke into two parts. Then, the flexural strength was calculated by using the Equation 3.2 (Callister 2010);

$$\sigma = \frac{3\mathrm{FL}}{2\mathrm{bd}^2}$$

(Equation 3.2)

Where;

- *F* is the load (force) at the fracture point (N)
- *L* is the length of the support span (mm)
- *b* is width (mm)
- *d* is thickness (mm)

The sample was then utilised for further testing including compressive strength, thin section analysis, ESEM and sorptivity (capillary absorption) evaluation. For the compression test, the broken halves were then regularised into 40 mm cubes (Cebeci et al. 1989) by cutting them with a STIHL saw.

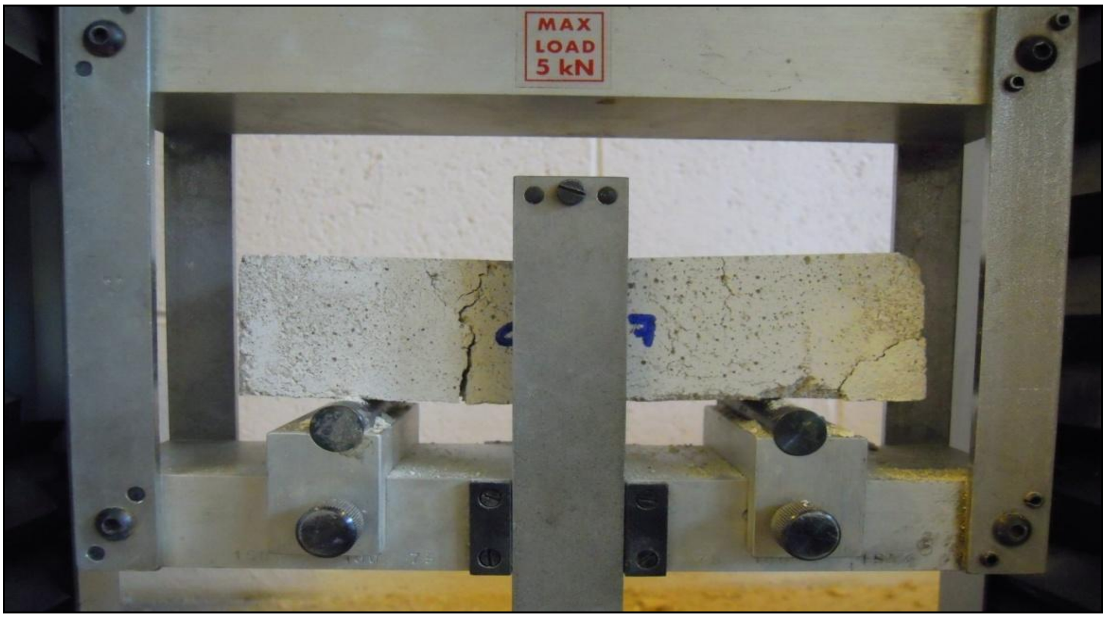


Figure 3.20: Flexural strength test

3.7.2 Compressive Strength

The compressive strength is the mechanism that is utilised to cross check the material performance with accepted wisdom. For this control to be relevant the specific batch proportions must be initially similar. Due to the experiment using lime binder from St. Astier, comparison was undertaken adopting data from St. Astier's physical and mechanical data results shown below (Table 3.7).

Table 3.7: Compressive strength after 28 days (Astier 2006)

St Astier NHL	Compressive strength after 28 days (N/mm^2)
NHL 2	1.36
NHL 3.5	1.47
NHL 5	2.00

This test also used the Lloyd's Universal Testing Machine (Model M5K) but adopted a different rig (Figure 3.21). The machine operates by applying a downwards pressure at a rate set by the operator, crushing the sample until failure. Graphs were plotted showing force applied against the distance that the arm applying the pressure has moved. The data produced illustrates the stress in the sample up to failure. Therefore, the strength of the specimen can be obtained.

Figure 3.21: Compressive strength test

3.8 Stage 5(c): Moisture Handling Characteristics: Sorptivity (capillary absorption)

The evaluation of capillary absorption for a material provides an insight into porous structure and volume (Benachour et al. 2008). Sorptivity is expressed as the '*tendency of a material to absorb and transmit water and other liquids by capillary*' (Hall and Hoff 2012). Sorptivity is sensitive to both the connectivity and the suction characteristics of the materials unlike the saturated permeability. The definition explains why this technique is ideally suited to this form of research and the test regime.

For this experiment, the unused remaining halves of the specimens from flexural test were used. The specimens were tested by adopting the direct gravimetric method. Prior to this, the specimens were dried in an oven at 105°C for half an hour. Then, the flat surface (opposite the fracture surface) was placed into 5mm of distilled water in a sealed container on non-absorbent plastic support (Figure 3.22).

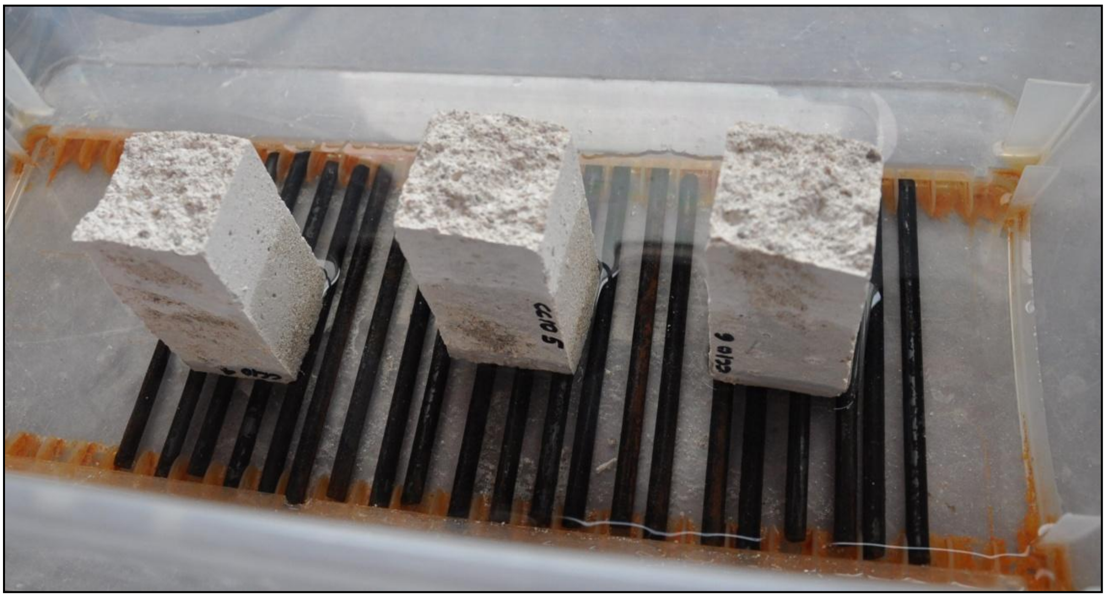


Figure 3.22: Sorptivity test

Hall and Hoff (2012) suggested that samples are sealed with epoxy resin to minimize loss of the absorbed liquid by evaporation and prevent lateral liquid absorption. However, in this research, the samples were not being sealed as the level of water contact with the samples was so minimal (1-2 mm) and due of short period of time, evaporation was considered as negligible.

The specimens were then weighed to ascertain the change in weight over specified time frame of 1, 3, 5, 10, 15, 30 minutes, the weight were taken not more than 30 seconds and the total time duration did not stop during these period. A minimum of 5 measured weight gain points were then plotted onto a graph with the water absorption measured in g/m^2 against the square root of time t$^{1/2}$. The sorptivity was then determined from the gradient of the slope (Equation 3.3) (Dias 2000);

$$i = k\sqrt{t}$$

(Equation 3.3)

In their research, De Oliveira et al. (2006) used kg/m^2/min$^{0.5}$ as unit for sorptivity coefficient, *k*. However, in this study, *k* values are expressed as volume basis; volume (mm^3) absorbed through across section (mm^2) per √min equal to mm/ min$^{0.5}$ according to works by Dias (2000), Hanzic and Ilic (2003) and Hall and Hoff (2012).

3.9 Stage 5(d): Micro-Structural Changes Analysis

A scanning electron microscope (SEM) produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition.

3.9.1 Environmental Scanning Electron Microscopy (ESEM) Analysis

The freshly fractured specimens were analysed using an Environmental Scanning Electron Microscopy (ESEM). This analysis was using XL30 ESEM™ LaB$_6$ machine. It uses ‘In HIVAC’ method with the column and specimen chamber are under high vacuum mode. The LaB$_6$ instrument is configured with a Lanthanum Hexaboride Electron source and the microscope runs in the Microsoft™ Windows NT™ setting.

This technique was utilised to produce images of a sample by scanning it with a focused beam of electrons (accelerating voltage of 20 kV). This enabled an evaluation of the surface characteristics of the materials to be determined including amorphous and crystalline products of hydration, pore structure and size distribution. Specimens were fractured and appropriate fragment sizes were used in the specimen chamber mounted rigidly on a specimen stub holder of 12.5 mm diameter (see Figure 3.23).

Specimens were carbon coated to be electrically conductive. Images were taken at 50, 100, 650, 1500, 2500, 5000 and 10000 magnification with a working distance (WD) of 10-15mm depending on the specimen’s size.

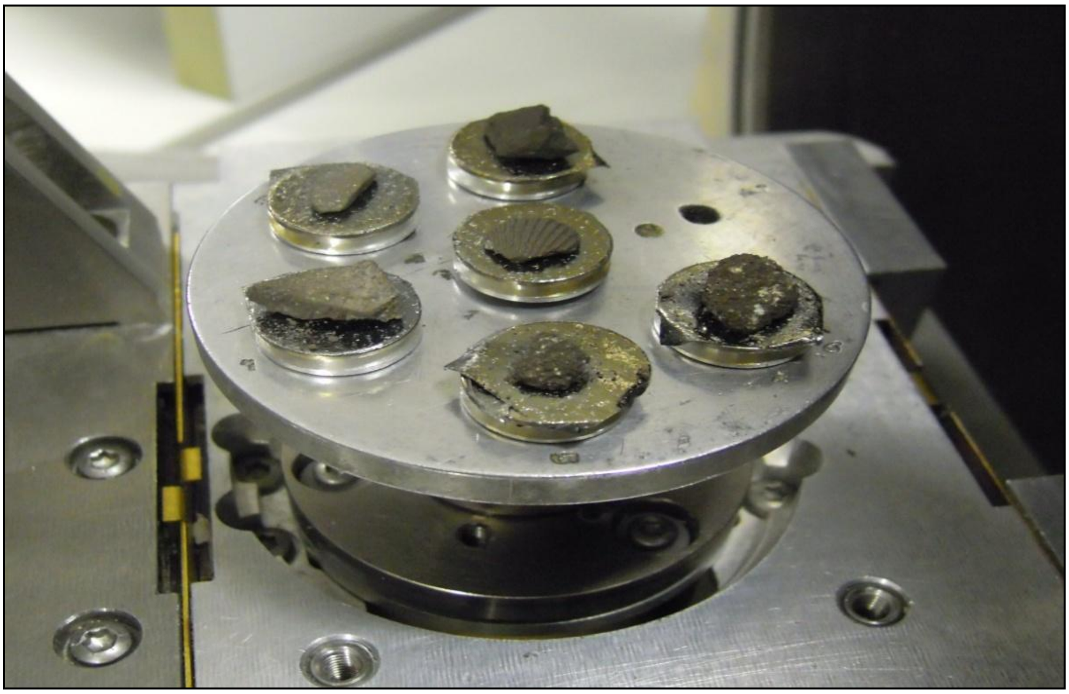
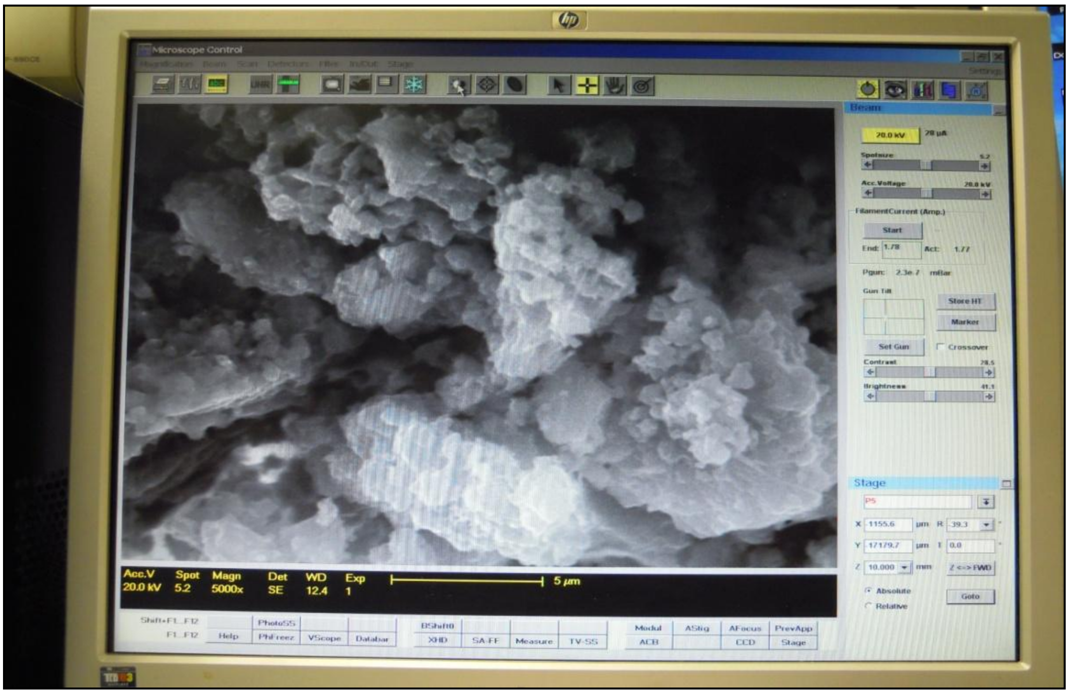


Figure 3.23: Carbon coated mortar fragment mounted on the stage inside the SEM



Acc.V	Spot	Magn	Det	WD	Exp
20.0 kV	5.2	5000x	SE	12.4	1

Figure 3.24: SEM image (in SE mode)

3.10 Summary of Chapter 3

The research methodology has been designed in order to achieve the four main objectives of the research. All tests were carefully prepared and organized to minimize error. Where ever possible reference and conformity to relevant British Standards and previous researchers' methods have been utilised to ensure rigour.

All results will be presented in Chapter 4. The results are arranged according to the four sub-sets of the testing stages i.e. chemical, physical, moisture handling and micro-structural changes characteristics. The modification of the NHL mortars adopting calcitic filler and their subsequent effects are divided into three sets of climate.

CHAPTER 4
RESULTS

4.1 Introduction

The results of both the control and calcitic filler modified Natural Hydraulic Lime (NHL) mortars are presented within this chapter. The modification of the Natural Hydraulic Lime mortars adopting calcitic filler and their subsequent effects have been divided into three sets of climates (including control climate). Each experiment was carried out for 56 days with time interval of 7, 14, 28, 42 and 56 as described in Chapter 3. In this chapter, the results are divided into two sections; (i) the effects of high temperature and humidity on lime mortar (Section 4.2) and (ii) modified mortar with calcitic fillers (Section 4.3 to 4.11). The calcitic filler effects on mortar physical performance were evaluated adopting the following methods;

a. Part One: The Chemical Properties of Modified Natural Hydraulic Lime Mortars
  - Moisture loss (Section 4.3)
  - pH value (Section 4.4)
  - Carbonation depth (Section 4.5)
  - Summary of Finding - Chemical Properties (Section 4.6)

b. Part Two: The Physical Properties of Modified Natural Hydraulic Lime Mortars
  - Flexural strength of each mortar type at each time interval (Section 4.7)
  - Compressive strength of each mortar type at each time interval (Section 4.8)
  - Sorptivity tests for each mortar type (Section 4.9)
  - Micro-structural changes through scanning electron microscopy (SEM) of 7 and 56 day interval (Section 4.10)
  - Summary of Finding - Physical Properties (Section 4.11)

Each set of climate experimentations were conducted individually for the complete duration (max 56 days) due to limited space within the curing cabinet. On the testing day, a dry cloth was used to cover each specimen after it has been taken out from the curing cabinet to avoid any contamination.

4.2 The Effects of High Temperature and Humidity on Natural Hydraulic Lime Mortar

In this section, the analysis of the first set of materials, examined the impact of high temperature and humidity on lime mortar. These results consist of 45 controlled specimens (un-modified mortar) cured in a controlled environment (temperature and humidity) of 20°C - 60% RH (20-60) and elevated climates of 27°C - 90% RH (27-90) and 33°C - 90% RH (33-90). Primary mortar parameters such as carbonation depth; flexural strength; compressive strength; and sorptivity are reported in this section. The results of the modified materials are reported after this (Section 4.3 to 4.11).

4.2.1 Carbonation Depth

Figure 4.1 presents the carbonation depth of mortars cured in a high temperature and humidity environment. This differs from the usual standard curing condition of 20°C - 60% RH. The figure illustrates that the 27°C - 90% RH samples carbonated significantly more rapidly than the other two conditions and attained full carbonation at 14 days. There is no carbonation depth difference between 20°C - 60% RH and 27°C - 90% RH from day 28 onwards. The 33°C - 90%RH has the slowest carbonation rate. Samples cured in 33°C - 90% RH condition has an approximate linear carbonation rate, with regression of R^2= 0.9649.

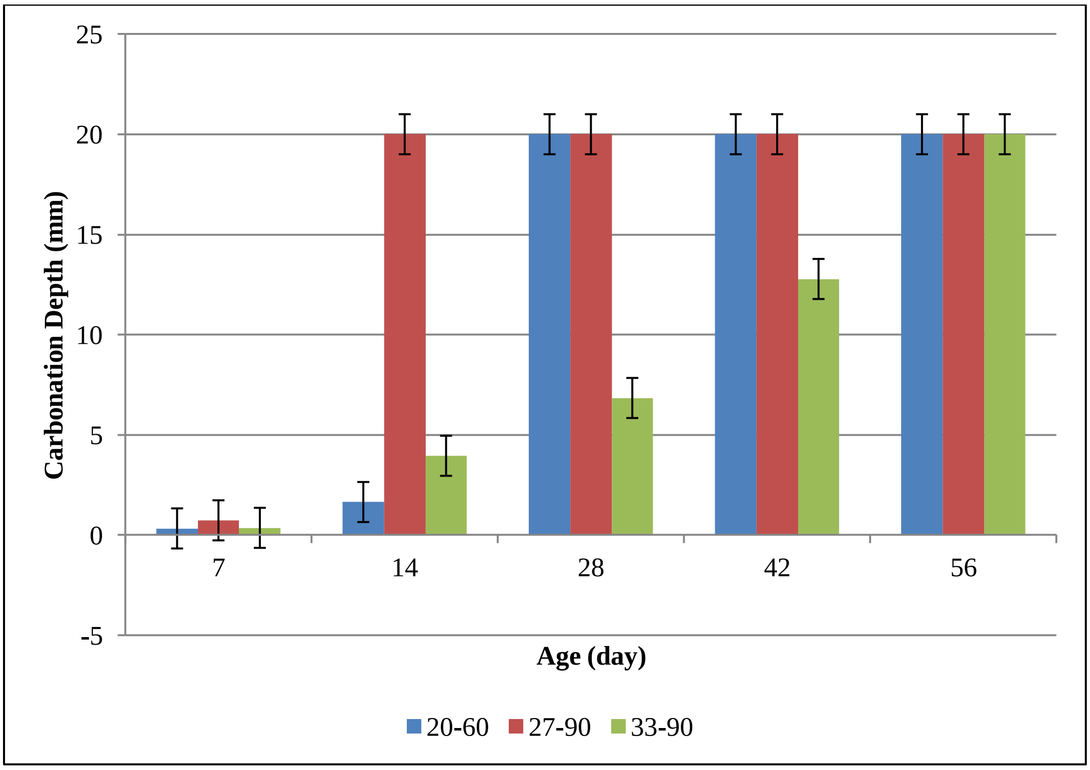


Figure 4.1: Carbonation depth of mortars in high temperature and humidity

4.2.2 Flexural Strength

Figure 4.2 shows the comparative flexural strength data for the control specimens subject to variations in the climate conditions (temperature and RH). In addition, the full test duration is reflected. The most effective curing climate for flexural development in the control specimens was 20°C - 60% RH. This data reflects both rapidity of early strength (at 7 days) and consistency of strength development throughout 56 days. At 56 days, the performance of 20°C - 60% RH was significantly greater than both the 27°C - 90% RH and the 33°C - 90% RH over the total test duration.

The strength development in the 27°C - 90% RH samples was anomalous. The specimens gained rapid early strength development (day 7 to 14) but subsequently lost strength after 28 days (61% loss). The specimens regained a constant strength after 42 days. Conversely, curing at 33°C - 90% RH was associated with initial linear flexural strength development up to 42 days but a clear decrease in strength from day 42 to the end of the experiment period was noted. From the experiment, 33°C - 90% RH specimens yielded the lowest flexural strength compared to other climate counterparts.

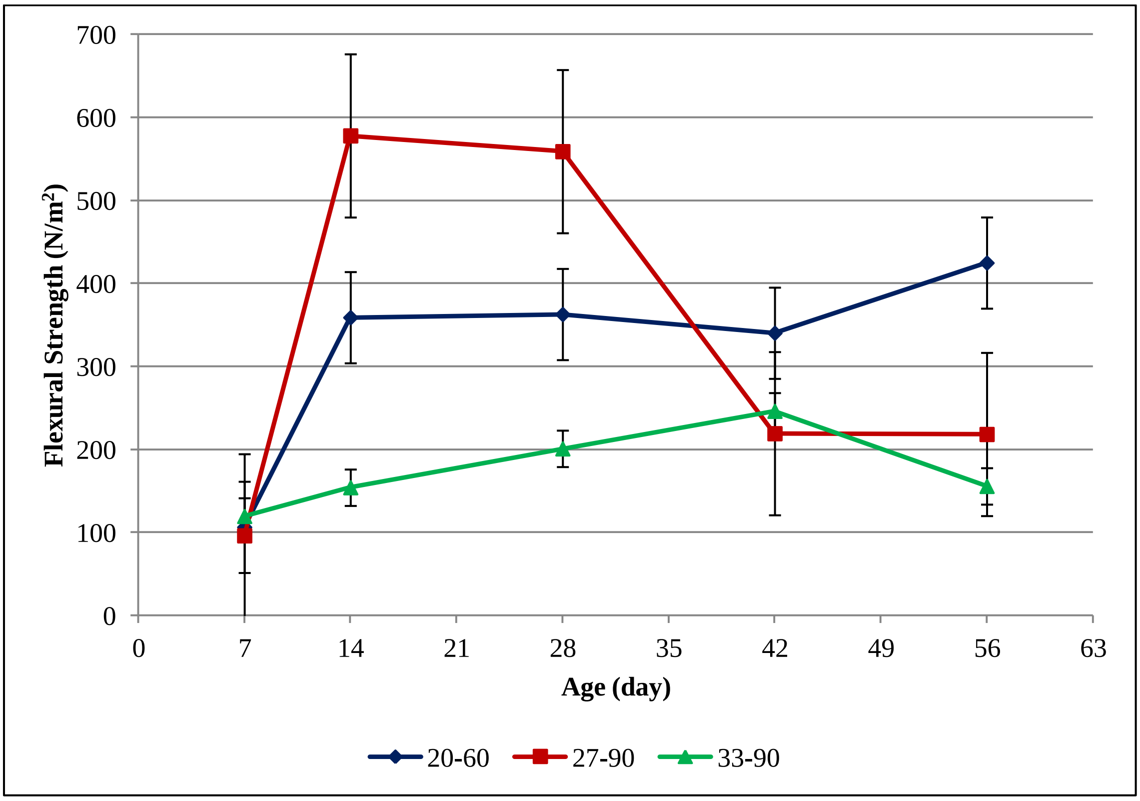


Figure 4.2: Flexural strength of mortars in high temperature and humidity

4.2.3 Compressive Strength

Figure 4.3 shows the comparative compressive strength of the control specimens in all climates over the complete test duration. Specimens cured in 27°C - 90% RH and 33°C - 90% RH conditions achieved a lower compressive strength than specimens cured in 20°C - 60% RH. Initially, the strength of the 20°C - 60% RH specimens' rapidly increased, surpassing the other two climates for a relatively short period (28 days). This was temporary with strength loss occurring at day 42. The specimens cured in 27°C - 90% RH exhibited the opposite to the 20°C - 60% RH. This manifested itself as initial low strength development, progressing to a pronounced rapid strength development at day 42 continuing until the end of the testing period.

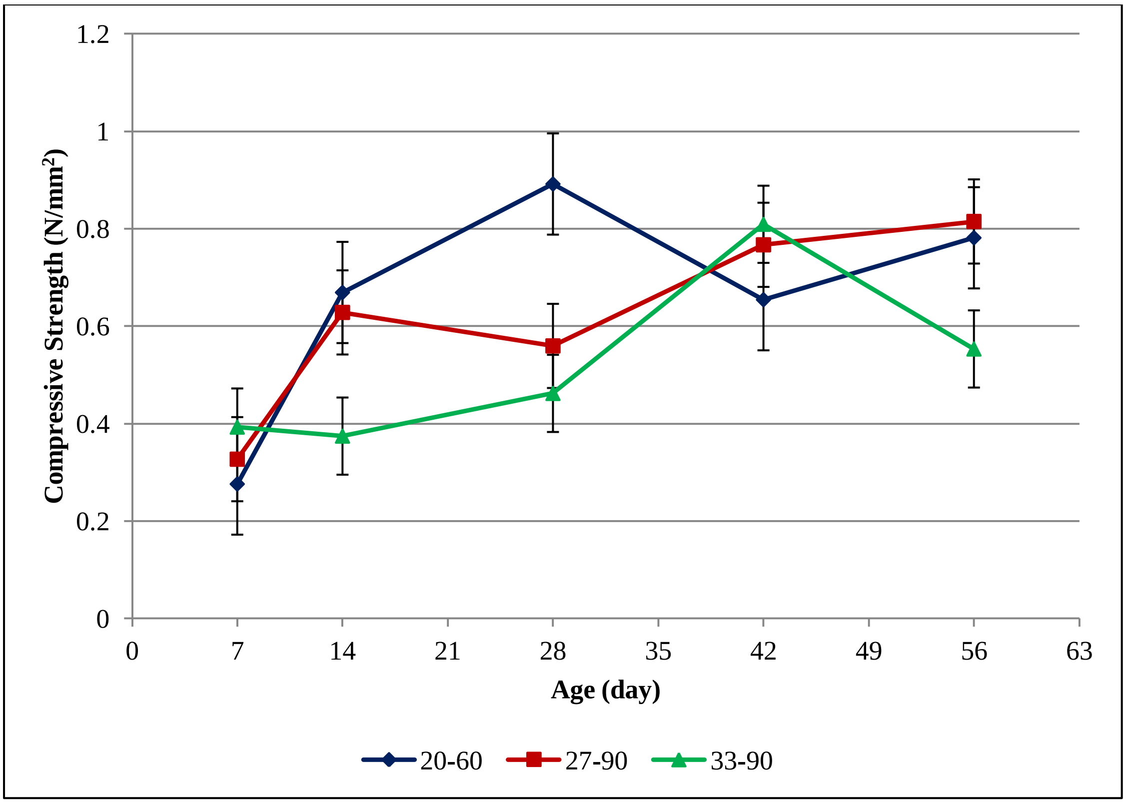


Figure 4.3: Compressive strength of mortars in high temperature and humidity

When evaluating the 7 day performance, 20°C - 60% RH samples had the lowest strength. The 27°C - 90% RH had the highest. The weakest initial and 56 day strengths were associated with the specimens cured in 33°C - 90% RH environments. This climate also showed the strength loss after 56 days of curing. The most effective (56 day strength) curing condition for the control mortar was 27°C - 90% RH based on its performance compared with other climates.

4.2.4 *Sorptivity Test*

Figure 4.4 provides the experimental data for the sorptivity of lime mortar control samples exposed to the three different climatic curing conditions. It is clear that the samples cured in 20°C - 60% RH condition had a denser structure than samples cured in 27°C - 90% RH and 33°C - 90% RH conditions and this is reflected in the high sorptivity values. Further analysis showed that 33°C - 90% RH samples attained the highest *k* values, indicating a large number of interconnected pores.

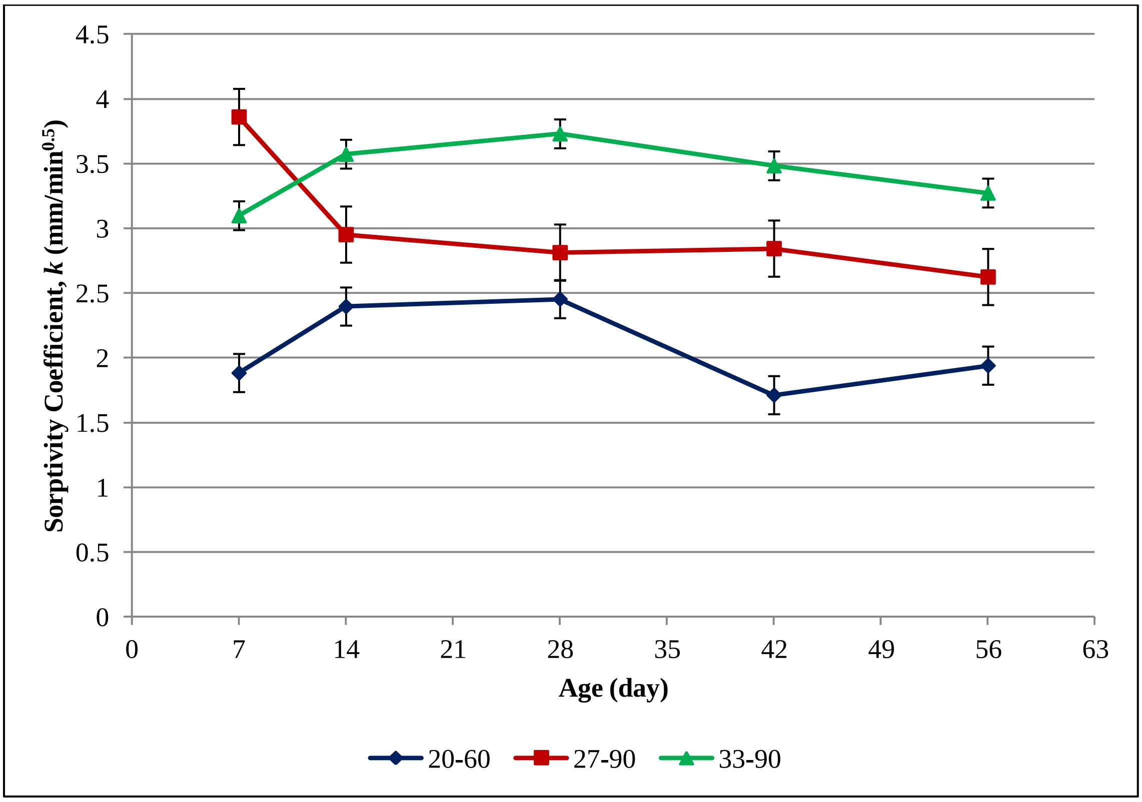


Figure 4.4: Sorptivity coefficient, *k* of mortars in high temperature and humidity

4.2.5 *Summary*

This study investigated the effects of curing the control samples of lime mortar in three high temperature and humidity conditions (20°C -60% RH; 27-90% RH; and 33-90% RH). There was a significant performance difference between samples cured in the standard conditions (20°C - 60% RH) and elevated temperature and humidity (27 - 90% RH and 33 - 90% RH).

The most striking result to emerge from the data is that, curing lime mortar in higher temperature and humidity caused adverse effects on strength and pore structure development. This is critical as the pore structure development greatly influences the properties of the hardened material in terms of strength, permeability and ultimately durability.

Comparison of the four tests reveal that mortar cured in higher temperature rapidly gained initial strength but this subsequently decreased with time. This can jeopardize the quality of mortar produced. This finding also goes some way to illustrate the difficulties in the current use of NHL materials in high temperature and humidity environments such as Malaysia.

Having established the trends for the control mixes, the effects on the mixes seeded with various fillers can now be described.

4.3 Moisture Loss

Figure 4.5, 4.6 and 4.7 illustrate the amount (in percentage) of moisture loss at time interval of 7, 28 and 56 days respectively in all curing climates. The figures indicate that there is a noticeable trend in performance of the modified mortar moisture loss that is higher than the control mortar samples. The seeded specimens with calcite substitution consistently lost more water than those without, indicating a possible increased sensitivity to curing for the seeded mortar.

The 20°C - 60% RH curing condition provides the smallest moisture loss of any of the mortars. The moisture loss of the mortar specimens in the 33°C - 90% RH curing conditions was the highest. It was observed that after prolonged exposure, the moisture loss becomes constant. Evaluating the comparison between the climates, it is evident that moisture loss increased in proportion with the increase in temperature and humidity.

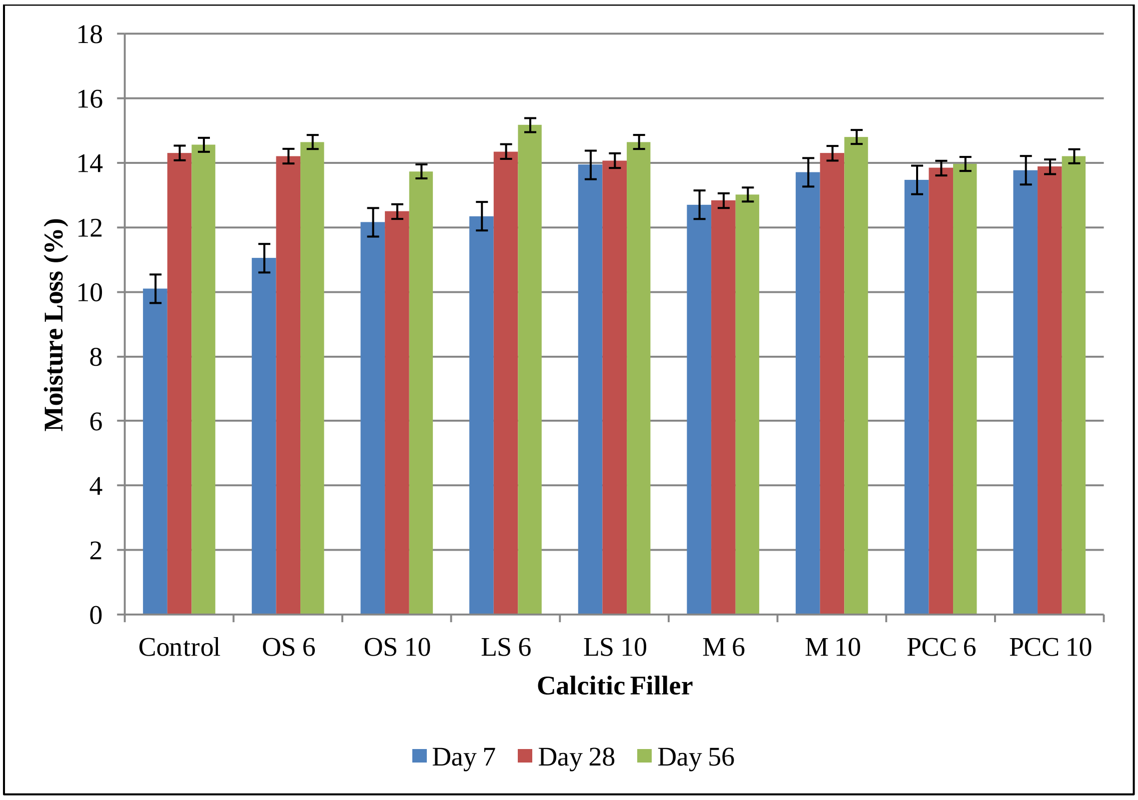


Figure 4.5: Water loss at 20°C-60% RH climate

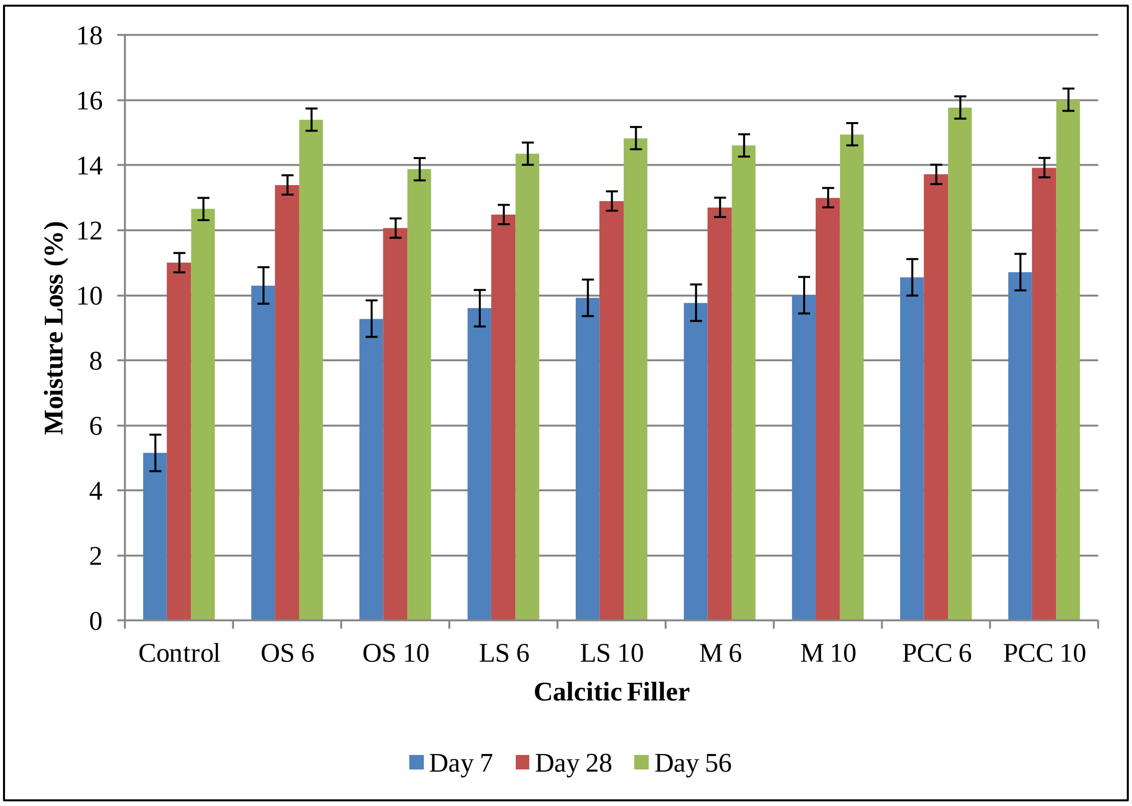


Figure 4.6: Water loss at 27°C-90% RH climate

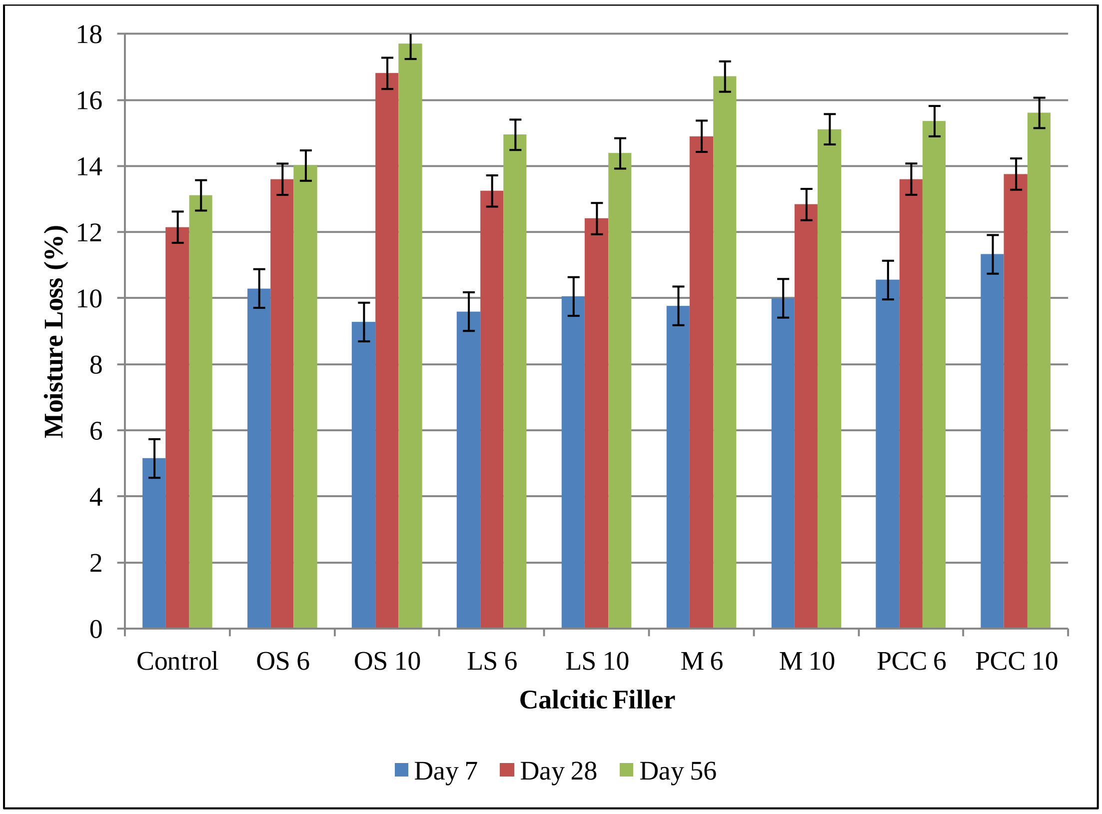


Figure 4.7: Water loss at 33°C-90% RH climate

4.3.1 Observations on Types of Calcite

Evaluating the performance of the samples exposed to 20°C - 60% RH, there was negligible difference between the specimens. The lowest moisture loss was associated with the control specimens and the highest was 6% limestone powder. It can be observed that moisture loss in 20°C - 60% RH occurred rapidly with an average of 12.5% for the first 7 days and a slower (smaller) moisture loss after that.

This also occurred with the samples subjected to 27°C - 90% RH and 33°C - 90% RH. The highest calcite fillers were precipitated 10% calcium carbonate and 10% oyster shells powder respectively. A major increase in moisture loss values was noted from day 7 to 56 in 27°C - 90% RH and 33°C - 90% RH environments.

4.4 pH

Five repeated readings were taken on the same day as the physical characteristics experiment. This was undertaken to avoid contamination or further carbonation of the sample (as discussed in Section 3.6.1). Table 4.1 below shows a pH development of each mortar at each time intervals in all three of climates.

Table 4.1 Mortar pH value at all time intervals

20°C – 60% RH							
Calcitic Filler	**Seeding (%)**	**pH**					
		0	**7 days**	**14 days**	**28 days**	**42 days**	**56 days**
Control	0	14	12	7	7	7	7
Oyster shells	6	14	12	7	7	7	7
Oyster shells	10	14	12	7	7	7	7
Limestone	6	14	12	7	7	7	7
Limestone	10	14	12	7	7	7	7
Marble	6	14	12	7	7	7	7
Marble	10	14	12	7	7	7	7
Precipitated CaCO$_3$	6	14	10	7	7	7	7
Precipitated CaCO$_3$	10	14	10	7	7	7	7
27°C – 90% RH							
Calcitic Filler	**Seeding (%)**	**pH**					
		0	**7 days**	**14 days**	**28 days**	**42 days**	**56 days**
Control	0	14	10	7	7	7	7
Oyster shells	6	14	10	7	7	7	7
Oyster shells	10	14	10	7	7	7	7
Limestone	6	14	10	7	7	7	7
Limestone	10	14	10	7	7	7	7
Marble	6	14	10	7	7	7	7
Marble	10	14	10	7	7	7	7
Precipitated CaCO$_3$	6	14	10	7	7	7	7
Precipitated CaCO$_3$	10	14	10	7	7	7	7
33°C – 90% RH							
Calcitic Filler	**Seeding (%)**	**pH**					
		0	**7 days**	**14 days**	**28 days**	**42 days**	**56 days**
Control	0	14	10	7	7	7	7
Oyster shells	6	14	10	7	7	7	7
Oyster shells	10	14	10	7	7	7	7
Limestone	6	14	10	7	7	7	7
Limestone	10	14	10	7	7	7	7
Marble	6	14	10	7	7	7	7
Marble	10	14	10	7	7	7	7
Precipitated CaCO$_3$	6	14	10	7	7	7	7
Precipitated CaCO$_3$	10	14	10	7	7	7	7

It is apparent from this table that all fresh mixed mortars had a pH of 14 on day of casting. These readings were taken approximately 20 minutes after batching. A pH of 14 is an indication of high proportion of calcium hydroxide ($Ca(OH)_2$) (Portlandite).

At day 7, all mortars in all climates still exhibited high pH values of 10 and 12. In 20°C – 60% RH, seven out of nine formulations showed pH values of 12; only precipitated

$CaCO_3$ (6% and 10% substitutions) had lower pH of 10. Conversely, all specimens cured in elevated climates recorded a pH reading of 10.

All the specimens' pH (including control) decreased to pH 7 after 14 days. As a mortar surface reacts with carbon dioxide in air, the pH of the surface is gradually reduced as the $Ca(OH)_2$ converts to calcite due to carbonation. Carbonation progressively lowers the pH in mortar. Carbonation also occurs in concrete but is generally low due to relative impermeability of the outer surface. In addition, decreasing the pH from 8 to 7 increases the maximum amount of Ca^{2+} ions.

4.4.1 Phenolphthalein

An additional technique to verify the pH level is to spray the mortar specimen with phenolphthalein. Phenolphthalein is an organic chemical reagent which stains materials magenta / purple when the pH is greater than 9.5. In this study, phenolphthalein spraying technique was used to measure the carbonation depth (see Section 4.5).

4.5 Carbonation Depth

Carbonation is the result of the dissolution of carbon dioxide (CO_2) in the mortar pore fluid and this reacts with calcium from calcium hydroxide and hydration products of calcium silicate hydrate to form calcite ($CaCO_3$). The use of phenolphthalein as a stain for determining the depth and extent of carbonation is based upon the pH of the mortar. Figure 4.8, 4.9 and 4.10 highlight the variation in effect of seeding materials on carbonation. The full results on carbonation depth can be referred to Appendix A. These variations possibly result from different compositions, physical forms and particle size of the seeding materials.

4.5.1 Effects of 20°C - 60% Relative Humidity Climatic Condition

Figure 4.8 shows carbonation depths (in mm) of all mortars. This depth was calculated numerically as the distance from the outer surface of the mortar to the start of the staining. Early stage (7 days) carbonation testing revealed little information on the effects of seeding additives as samples were held within moulds for the first 7 days of curing, with only a single face exposed and therefore subject to carbonation. At day 7, the control mortar specimens had a higher carbonation value than all modified materials. In addition, it was observed that modified mortars with 10% calcitic filler experienced a higher rate of carbonation compared to 6%. At day 14, the carbonation rate of control specimens were superseded by modified mortars.

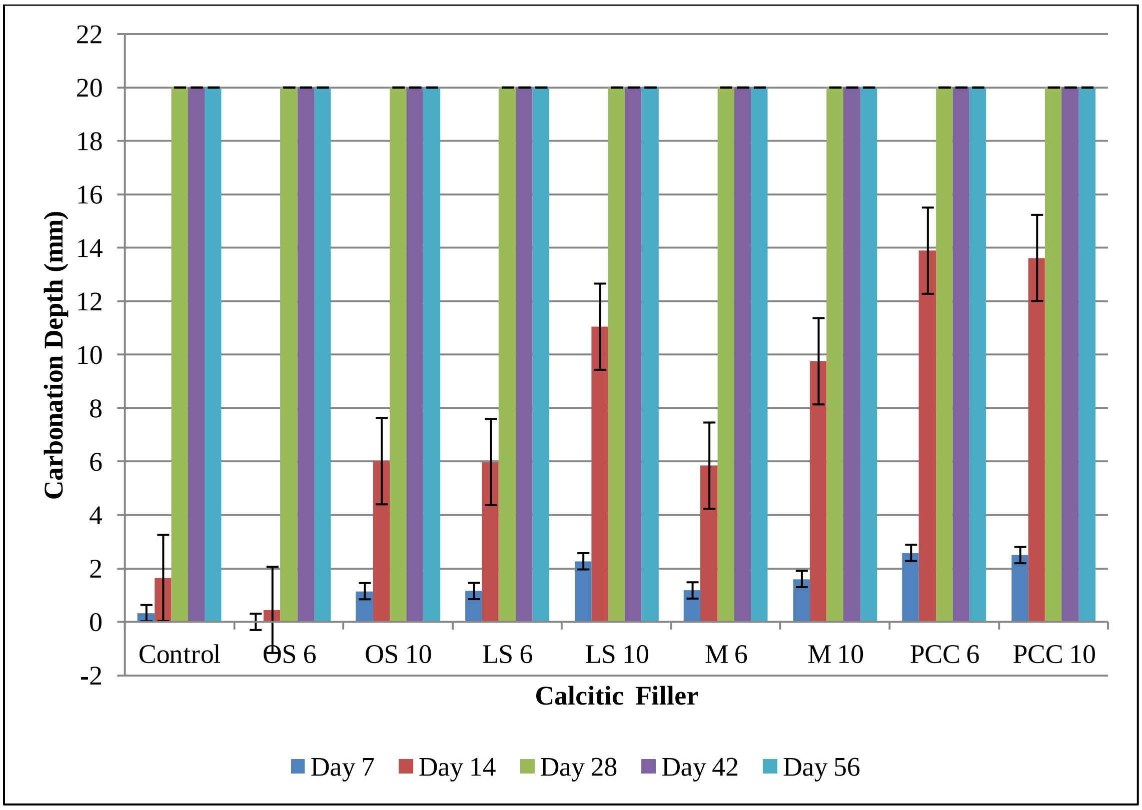


Figure 4.8: Carbonation depth all mortar for samples (20°C - 60% RH)

4.5.2 Effects of 27°C - 90% Relative Humidity Climatic Condition

Figure 4.9 shows the phenolphthalein stain results on 7 day old modified mortars. Figure 4.10 represents the carbonation depth (in mm) of each mortar over the specified time intervals. All mortars showed relatively low early carbonation rate up to 7 days. The 6% oyster shells exhibited lower carbonation rates when compared to 10% oyster shells. This was also observed in the limestone samples. Conversely, a concentration of 6% marble and 6% precipitated calcium carbonate exhibited similar carbonation rates with their 10% counterparts. After 14 days the control and oyster shells both achieved full carbonation irrespective of carbonate filler concentration. All specimens achieved full carbonation by 28 days.

Figure 4.9: Phenolphthalein stains on 7 day old modified mortar cured in 27°C – 90% RH. (a) Oyster shell, (b) limestone, (c) marble and (d) precipitated calcium carbonate

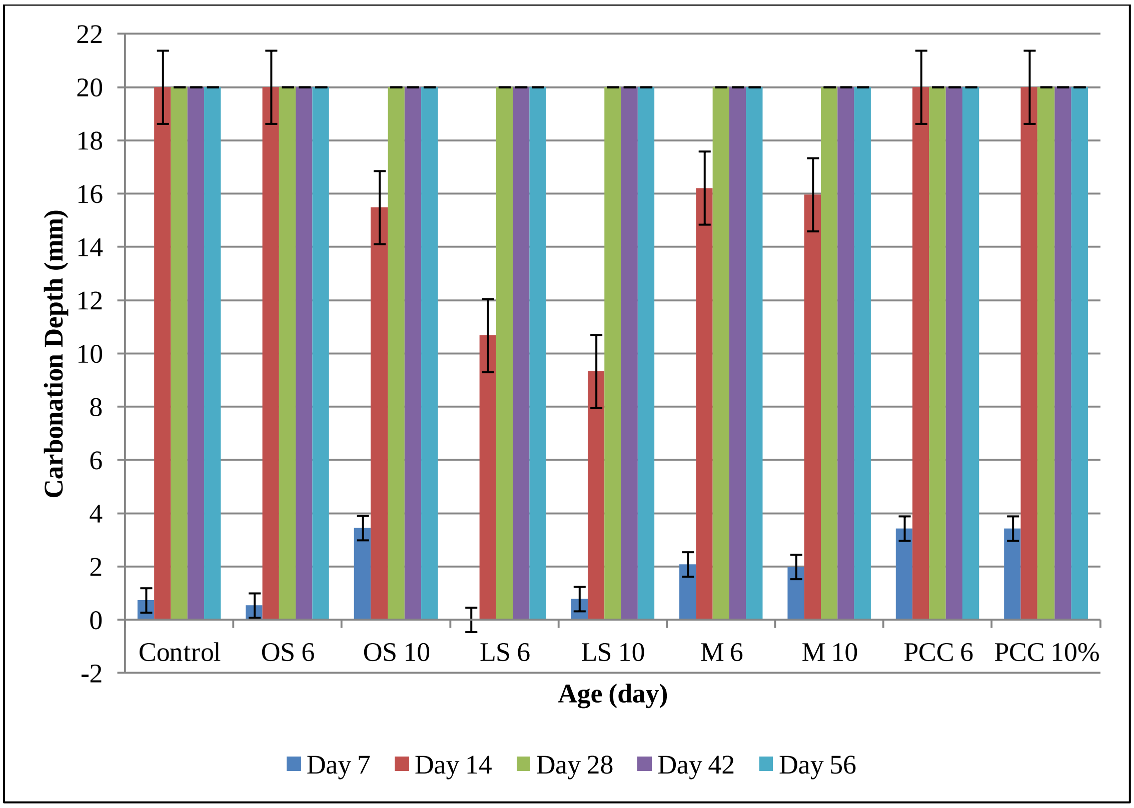


Figure 4.10: Carbonation depth all mortar for samples (27°C - 90% RH)

4.5.3 Effects of 33°C - 90% Relative Humidity Climatic Condition

The Figure 4.11 and 4.12 illustrate the phenolphthalein stain results on 7 and 14 day old modified mortar respectively. Figure 4.13 represents the carbonation depth (in mm) of each mortar over the specified time interval. Early stage (7 days) carbonation testing reveals little information on the effects of seeding additives included in the samples. This was associated with the samples being held in the moulds for the first 7 days of curing, with only a single face being exposed to air. Therefore this was the only surface that could possibly be subjected to carbonation.

Mid-study measurements (28 days) showed all the seeding materials had a positive influence, with clear advancement of carbonation depths, compared with the un-seeded control samples. A positive carbonation effect was most noticeable in the limestone seeded materials. The positive effects of the oyster shells were however short lived, with control samples exceeding carbonation of oyster shell seeded samples by 42 days. Limestone appears to be the only material that exhibited any significant, prolonged impact on carbonation depth. The increase in carbonation depth achieved with calcium carbonate seeding at 42 days is likely to be within the error of measuring. All samples achieved full carbonation by 56 days.

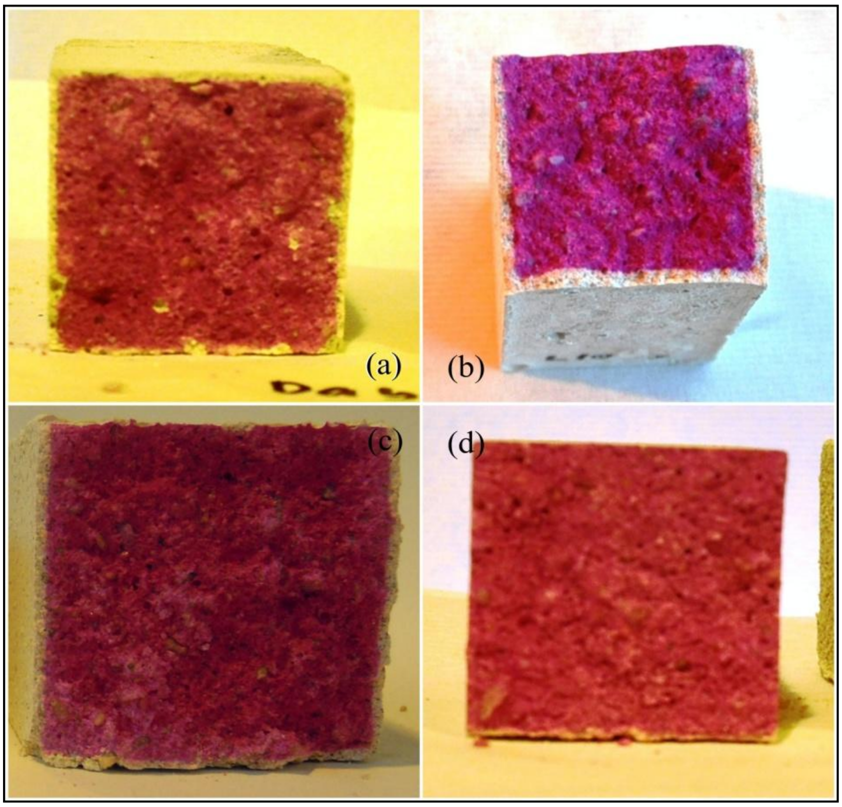


Figure 4.11: Phenolphthalein stains on 7 days old modified mortar cured in 33°C – 90% RH. (a) Oyster shell, (b) limestone, (c) marble and (d) precipitated calcium carbonate

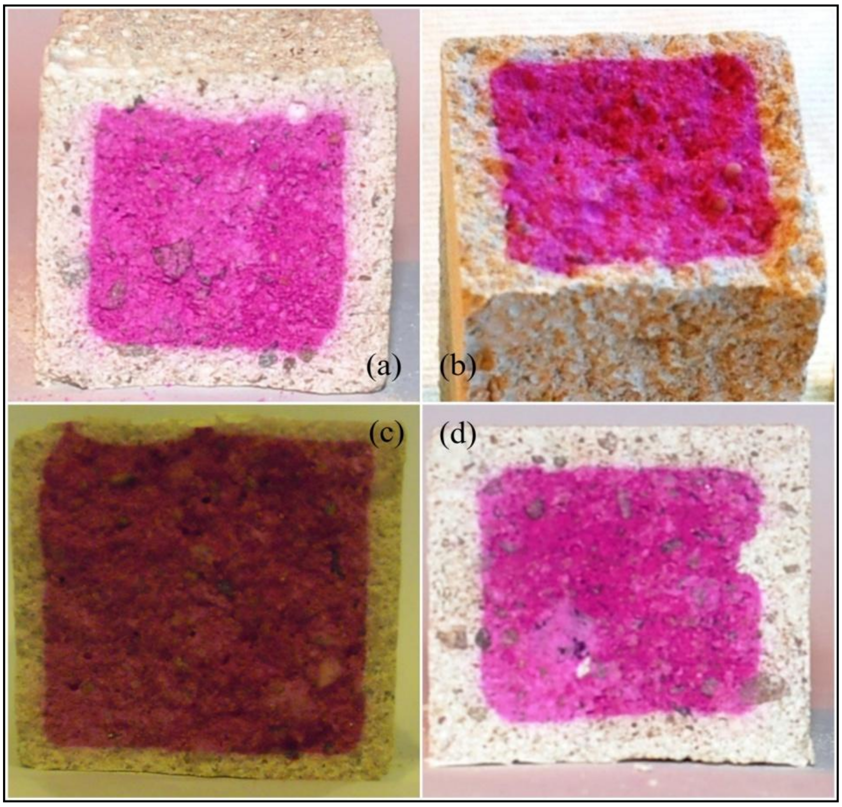


Figure 4.12: Phenolphthalein stains on 14 days old modified mortar cured in 33°C – 90% RH. (a) Oyster shell, (b) limestone, (c) marble and (d) precipitated calcium carbonate

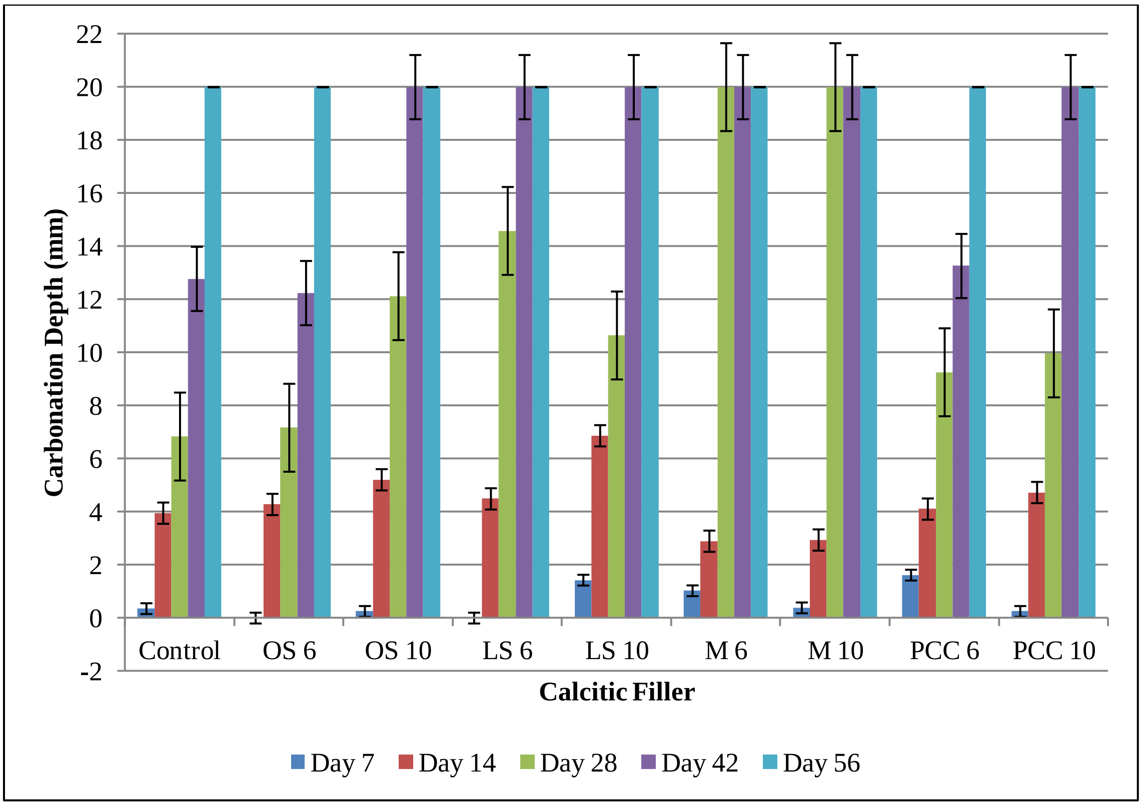


Figure 4.13: Carbonation depth all mortar for samples (33°C - 90% RH)

4.5.4 Comparison between Calcite Fillers in Early Development (7 and 14 days)

Based on Figure 4.8, 4.10 and 4.13, it can be concluded that the best curing condition for carbonation is associated with 27°C - 90% RH while the worst curing condition is 33°C - 90% RH. When cured at higher temperatures, the mortar lost moisture faster. This reduces the amount of water present for portlandite to dissolve into thus inhibiting the carbonation process. The inclusion of additional water through spraying helped to stimulate the hydration process and this can be seen as carbonation accelerated after 14 days.

At day 7, oyster shells 10% and precipitated calcium carbonate (6% and 10%) achieved the highest carbonation rates. At days 14 the control specimens achieved full carbonation along with 10% oyster shells and both 6% and 10% seeding adopting precipitated calcium carbonate. It can be observed that the best calcitic filler for carbonation is precipitated calcium carbonate (PCC).

4.6 Summary of Finding on Chemical Properties

The chemical tests enabled the identification and comparative analysis of different rates of carbonation of the control and modified mortar. However, the data obtained was unable to give information regarding the nature of the carbonation reaction i.e. carbon dioxide concentration. It can be summarized that from the chemical characteristics investigations;

a. Fresh mortars have higher pH values that reduce over time; attributed to progressing carbonation.

b. Modified mortars are more sensitive to curing than those without.

c. Curing at higher temperatures greatly accelerates the hydration reaction of the mortar. This appears more pronounced in those mortars with mineral inclusions.

d. These results highlight the variation in effect of seeding materials on carbonation.

4.7 Flexural Strength

The three point flexural test technique was used to conduct this investigation. The results obtained from this testing method are sensitive to specimen loading geometry and strain rate.

Figure 4.14, 4.15 and 4.16 represent the flexural strength of each mortar over the test period. The calculations were based on Equation 3.2 (established in Section 3.7.1) and the values of the parameters are stated in Table 4.2;

Table 4.2: Flexural strength test measurement

Parameters	**Measurement (m)**
Length of the support span, L	0.1016
Specimen width, b	0.04
Specimen thickness, d	0.04

All samples exhibited an elevated flexural strength at 7 days that subsequently decreased at 14 days. The samples flexural strength subsequently decreased at 14 days upon dehydration.

The seeded materials exhibited higher flexural strength than the control mortar throughout the test period. This was particularly pronounced at 56 days. It is unclear why the control sample displayed a decline in flexural strength at 56 days but this may be a reflection of changes (an increase) in pore structure associated with carbonation although this does not correlate with the formation of products of hydration, which would also be expected within this time period (42-56 days).

4.7.1 20°C - 60% Relative Humidity Climatic Condition

In the 20°C - 60% RH climate (see Figure 4.14), seven formulations gained higher flexural strength than the control mortar at 7 days old. All mortars exhibited rapid strength development from day 7 to day 14. After 14 days a constant development plateau was observed in the graphs. Oyster shells, limestone and marble exhibited stable strength development. The weakest mortars were 6% limestone and 6% precipitated calcium carbonate with a 40% lower strength than the control specimens. 10% precipitated calcium carbonate yielded the greatest strength (50% more than control specimens) at 28 days but the performance was short-lived as the specimens experienced a steep strength reduction by 31.5% at day 42, becoming constant at day 56.

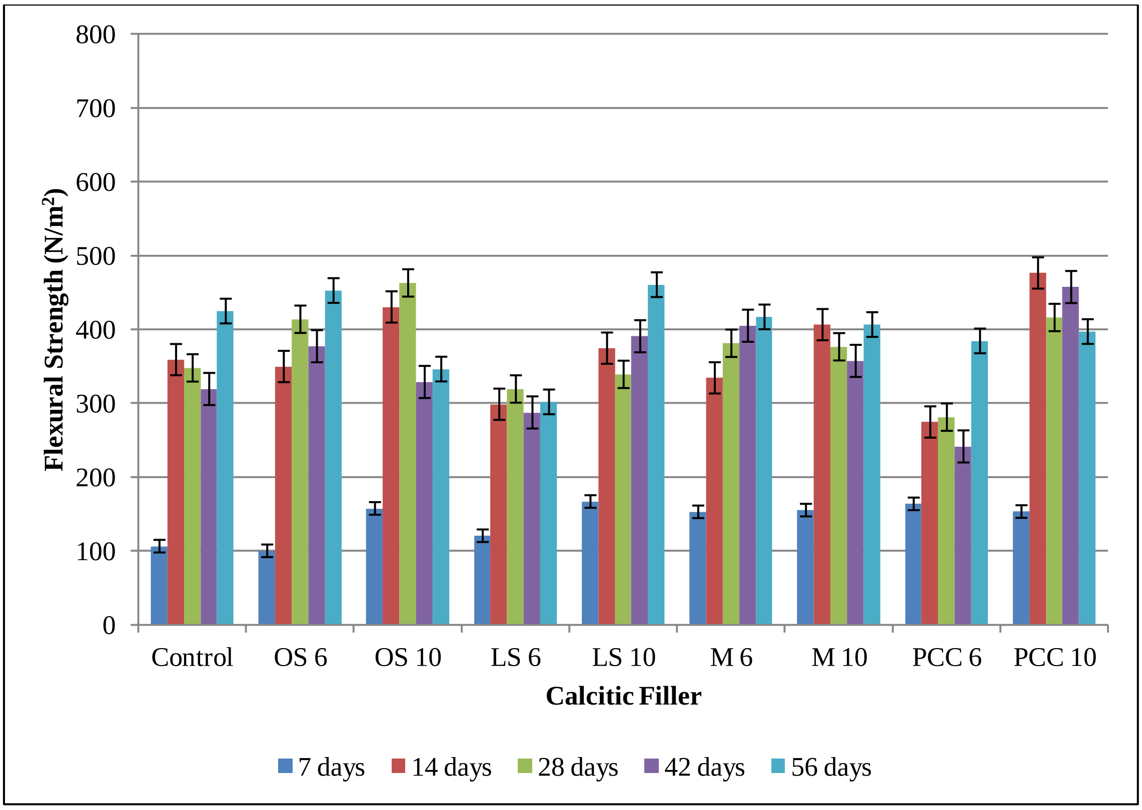


Figure 4.14: NHL mortars flexural strengths at 20°C - 60% RH

4.7.2 27°C - 90% Relative Humidity Climatic Condition

For 27°C - 90% RH (see Figure 4.15), a trend of relatively rapid strength development of all mortars can be observed from 7 to 14 days. After this eight out of nine modified mortars suffered a strength loss from 14 to 42 days. However, after day 42, the strength increased. Only 10% oyster shells were still gaining strength up to day 28 days period. However, it was temporary as 10% oyster shells lost strength after day 28 onwards, contrary to other specimens. From the data, 10% marble was the weakest mortar and the strongest mortar was 10% precipitated calcium carbonate (67.3% higher than control).

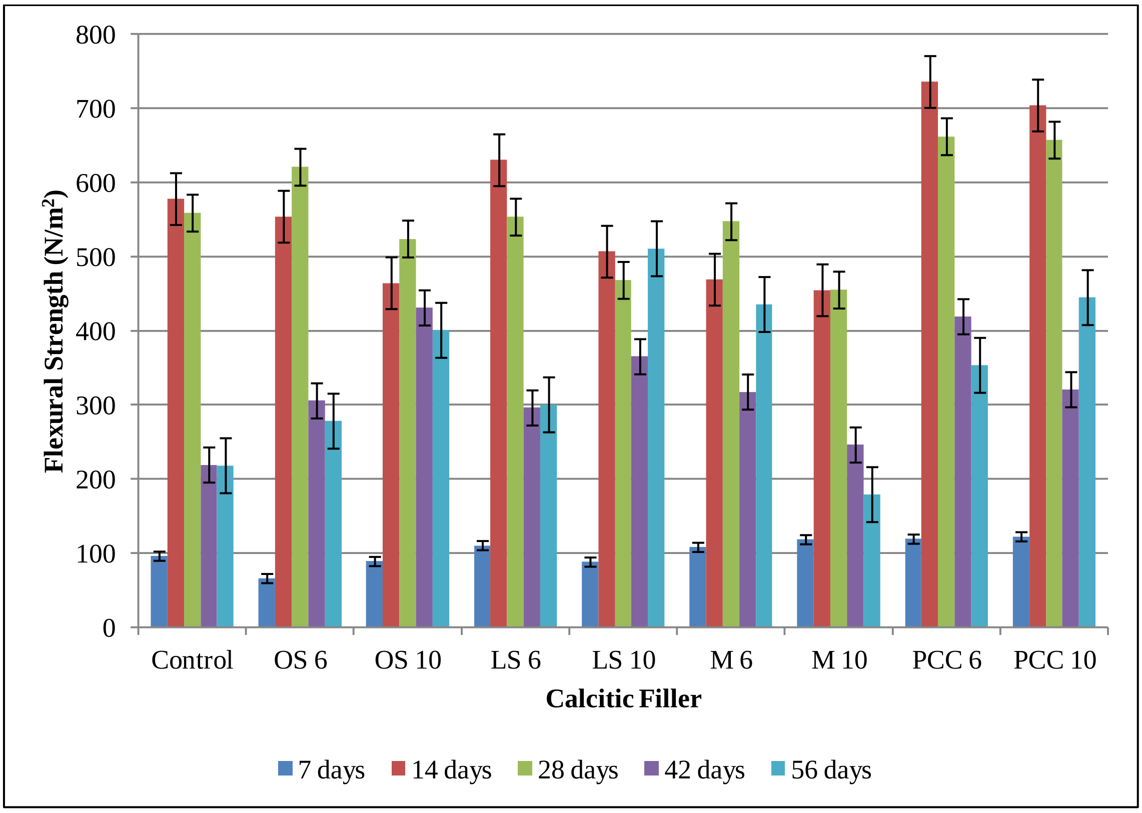


Figure 4.15: NHL mortars flexural strength at 27°C - 90% RH

4.7.3 33°C - 90% Relative Humidity Climatic Conditions

In 33°C - 90% RH climate (see Figure 4.16), all modified mortars gained strength within the test duration compared to controlled mortar. The control mortars gained constant strength up to 42 days but slowly lost strength after that. 6% and 10% marble did not gain any strength after 14 days and produced a constant strength (a plateau reading) until the end of the study. From the data obtained, the strongest mortar was 10% precipitated calcium carbonate with 62% more strength compared to control at 28 days. Conversely, the weakest mortar compared to other calcitic filler formulations was

6% oyster shells, which gained 15.5% more flexural strength compared to control at 28 days.

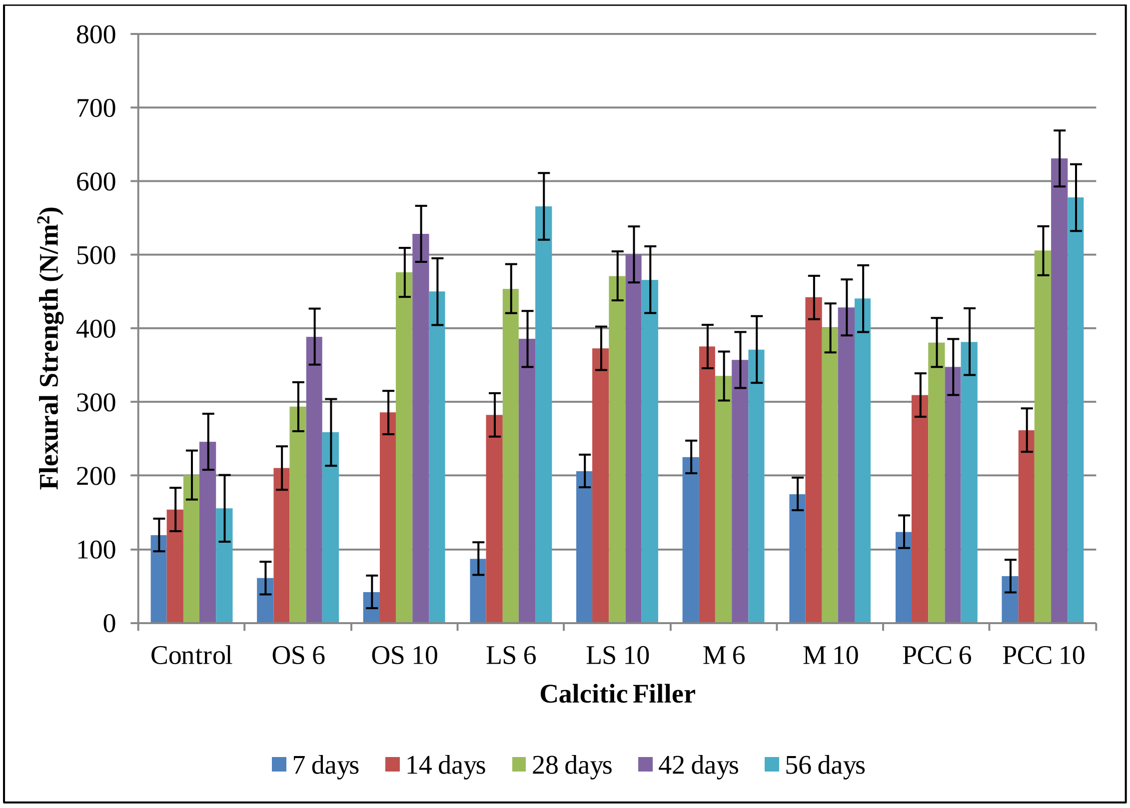


Figure 4.16: NHL mortars flexural strengths at 33°C - 90% RH

4.7.4 Non-symmetrical Cracks

From observations made during the 7 day flexural strength test, almost 40% of the total specimens in all climates suffered a non-symmetrical (¾) cracking during loading (see Figure 4.17).

Figure 4.17: Specimen with ¾ crack during flexural strength test at day 7

4.7.5 Flexural Strength Based on Climates

Experimental results indicate a clear difference between the seeded specimens and the control samples with regards to the development of flexural strength. Figure 4.2 in Section 4.2.2 shows the comparative flexural strength data for the control specimens and all climate variations for the full test duration. The most effective curing climate for non-modified mortar is 20°C - 60% RH.

4.7.6 Flexural Strength Based on Calcitic Fillers

Four types of calcitic fillers were used in this study; oyster shells powder, limestone powder, marble powder and precipitated calcium carbonate. Each type was subdivided into two amount of seeding material, namely; 6% and 10%. From the data obtained, 88% of the total specimens in all climates with 10% of seeding recorded a higher flexural strength value than their 6% seeding amount counterpart.

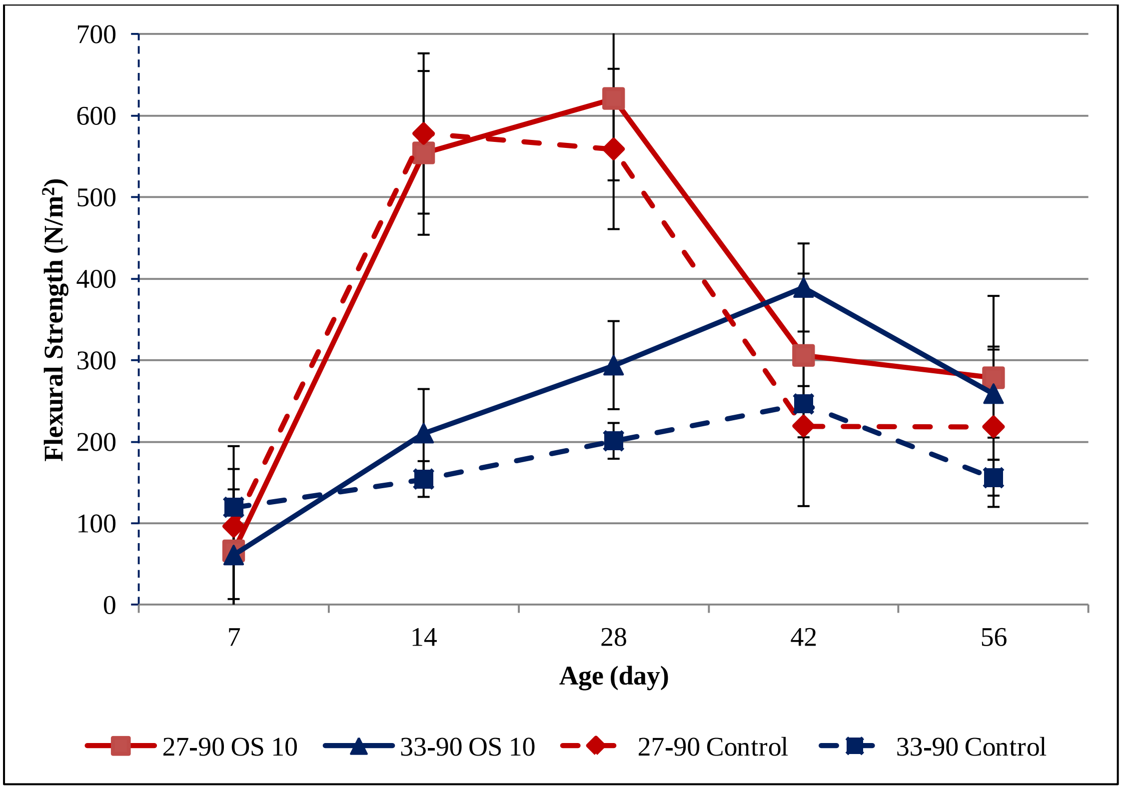


Figure 4.18: Flexural strength of oyster shells 10% specimens in elevated climates

Figure 4.18 above shows a comparative performance between flexural strength of 10% oyster shells specimens in elevated climates (27°C - 90% RH and 33°C - 90% RH) over the complete test duration. Generally, modified mortars with oyster shells have the same pattern with the un-modified mortars. Even though control samples yielded a higher strength for the first 14 days, they slowly lost strength post 28 days. It has been shown that in elevated temperatures and humidities, the strength loss can be reduced. In 27°C - 90% RH climate mortars with oyster shells have 28% more strength than controlled mortars.

The same strength development between controlled and PCC mortars are observed in 33°C - 90% RH. Both specimens gained strength from initiation of the curing period. Climate oyster shells can increase the mortar strength by 38% (based on day 42 value). However, both specimens lost its strength at day 42.

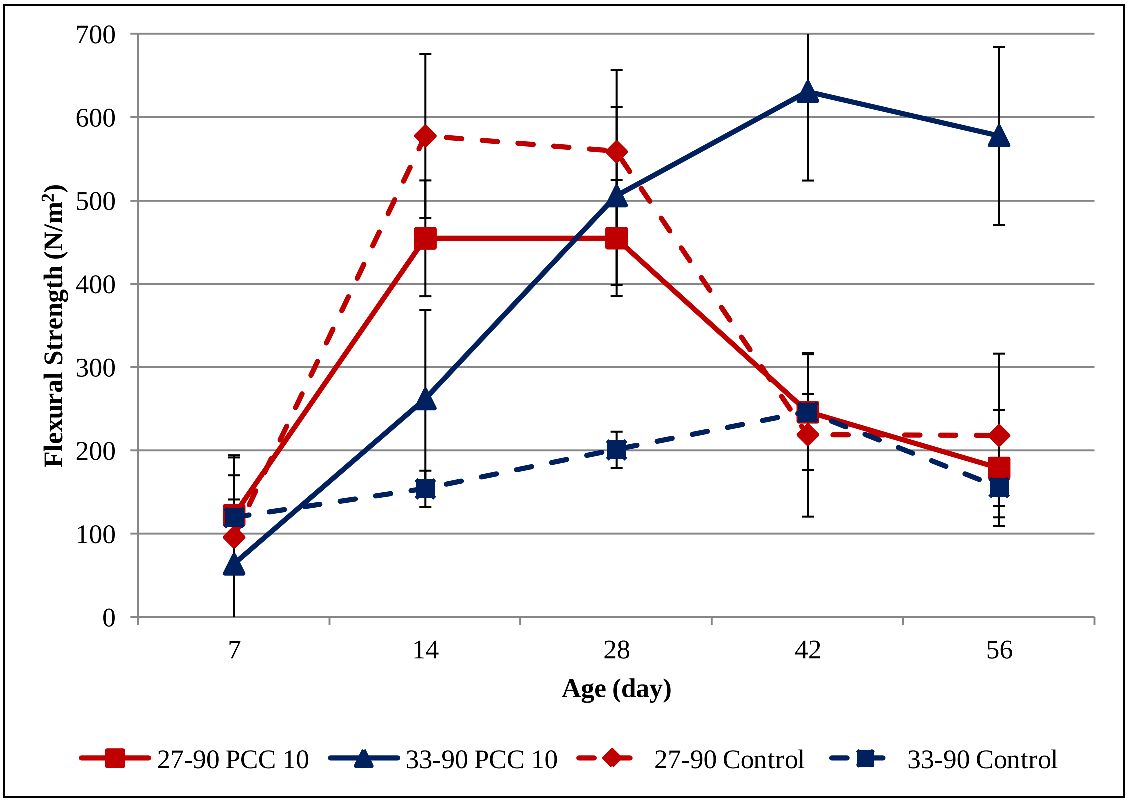


Figure 4.19: Flexural strength of precipitated $CaCO_3$ 10% specimens in elevated climates

Figure 4.19 above shows comparative performance between the flexural strength of 10% precipitated calcium carbonate specimens in elevated climates (27°C - 90% RH and 33°C - 90% RH) over the complete test duration. Both un-modified and modified specimens show a similar strength development pattern.

Overall, 10% precipitated calcium carbonate gained lower strength than the controlled specimens in 27°C - 90% RH. In addition, 10% precipitated calcium carbonate suffered a strength loss after 28 days. From the graph, it is evident that seeding is not effective in 27°C - 90% RH although the strength pattern is similar to control samples.

On the contrary with specimens in 33°C - 90% RH, the precipitated calcium carbonate filler in 33°C - 90% RH exhibited positive flexural strength results associated with curing in high temperature and high humidity condition. From the results, it is evident that precipitated calcium carbonate is suitable as seeding materials in mortar cured in high temperature and humidity.

4.8 Compressive Strength

Figure 4.20, 4.21 and 4.22 represent the compressive strength of each mortar at each time interval. The control specimens exhibited a significant loss of strength between 42 and 56 days unlike the seeded mortars which continued to gain strength.

4.8.1 20°C - 60% Relative Humidity Climatic Condition

Based on the Figure 4.20, it can be seen that all modified mortars with calcitic fillers have higher early strength values up to 14 days than the un-modified mortar. During 14-28 day period, 10% oyster shells and precipitated calcium carbonate gained the highest strength while the other calcitic fillers had a constant strength development until the end of the testing period (plateau value).

However, the performance of 10% oyster shells and 10% precipitated calcium carbonate were temporary as both calcite materials suffered strength loss of 11% and 26.7% respectively. Conversely, both calcite materials gained low level strength development until the end of the test. Evaluating the unmodified mortar samples, the strength development stopped after 14 days.

The strongest mortar was 10% precipitated calcium carbonate that gained 61.3% more strength compared to control specimens at 28 days. Mortar with 6% oyster shells, 6% marble and 6% limestone seeding materials exhibited no significant results compared to control specimens over the test duration.

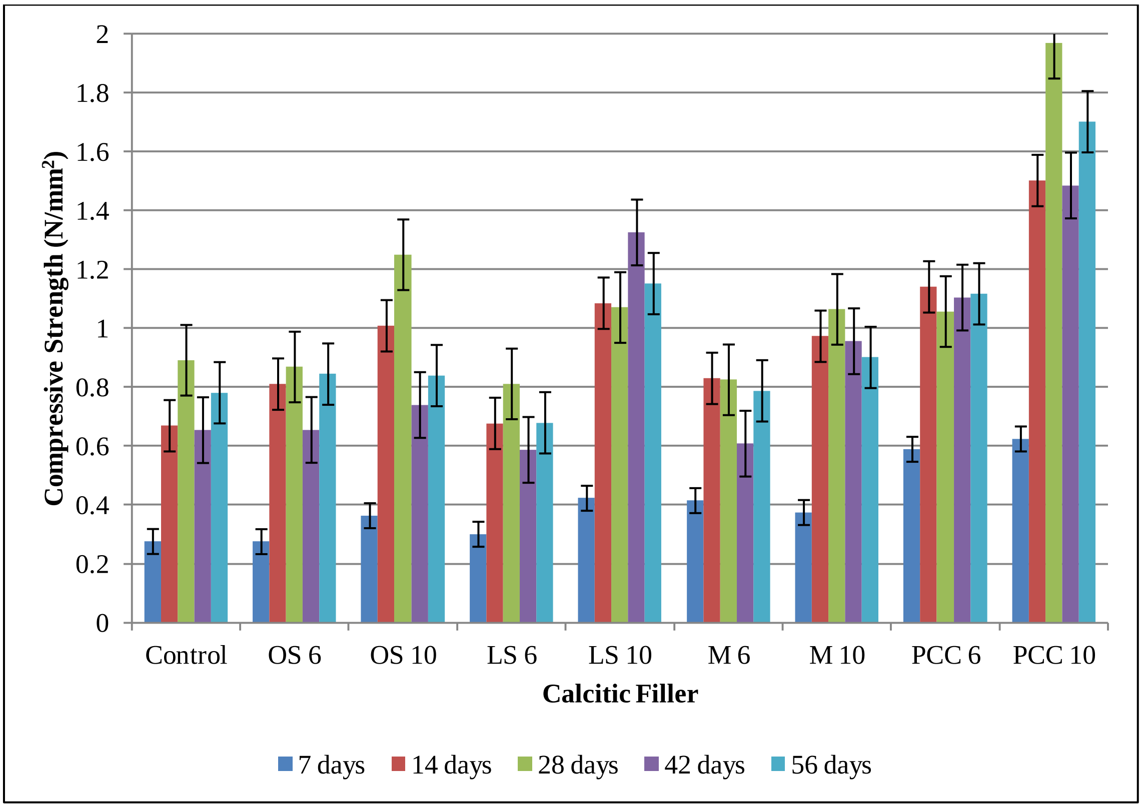


Figure 4.20: Compressive strengths at 20°C - 60% RH

4.8.2 27°C - 90% Relative Humidity Climatic Condition

Figure 4.21 represents the compressive strength in 27°C - 90% RH climate. Between 7 - 14 days, it can be seen that all modified mortars exhibited rapid early strength gain. This is reflected in the steep positive gradient of the graph line. At 28 days, 6% oyster shells and 6% marble had a 34% and 40% respective strength loss. At 42 days only the 10% precipitated calcium carbonate continued to gain strength until the end of the testing period. From the overall data, precipitated calcium carbonate in both seeding amounts achieved the strongest mortars in comparison to others.

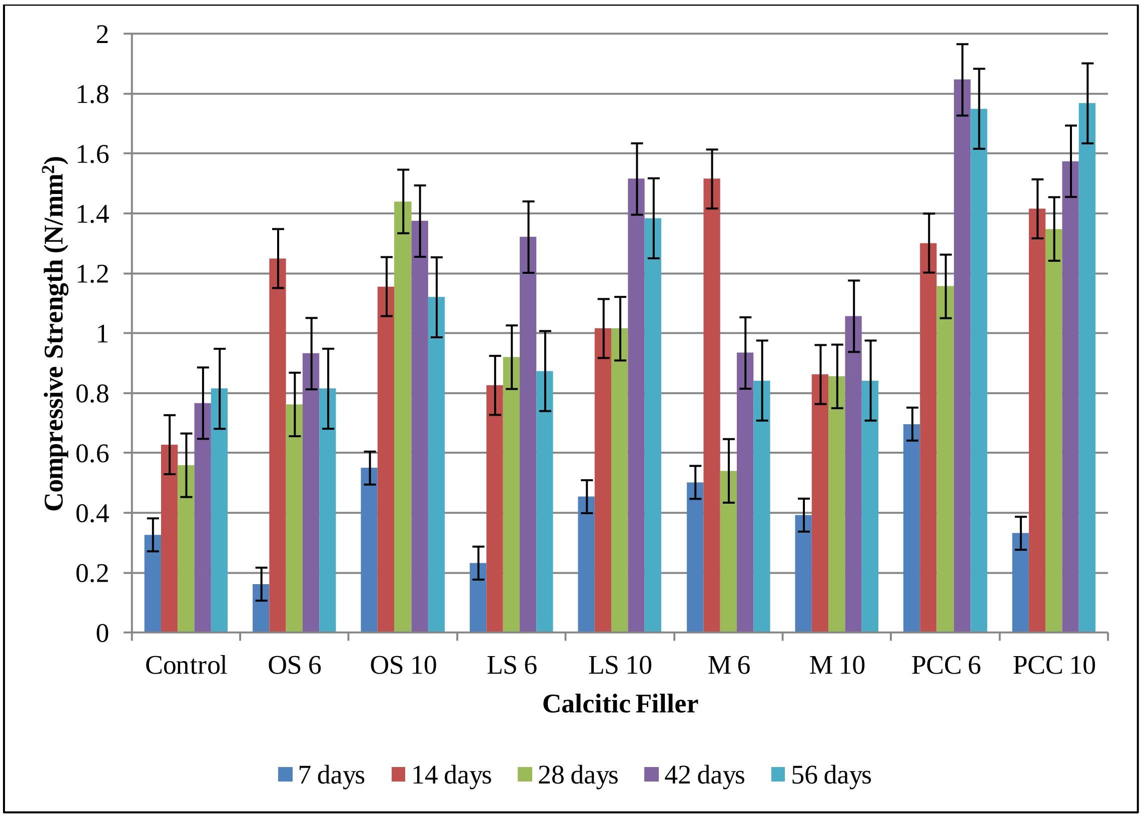


Figure 4.21: Compressive strengths at 27°C - 90% RH

4.8.3 33°C - 90% Relative Humidity Climatic Condition

Figure 4.22 represents the compressive strength in 33°C - 90% RH climate. All mortars experienced a slow early strength development up to 28 days. However, most of the mortars exhibited rapid changes in strength gain, or strength loss after 28 days up to the end of the testing period.

The control specimens had a strength loss of 27.3% at day 56. Marble did not contribute any significant results (strength development stopped at day 14) in the test even though the strength value it achieved was higher than the control specimens. The strongest mortar in this test was precipitated calcium carbonate, gaining 71.9% more strength than control specimens at the end of the test.

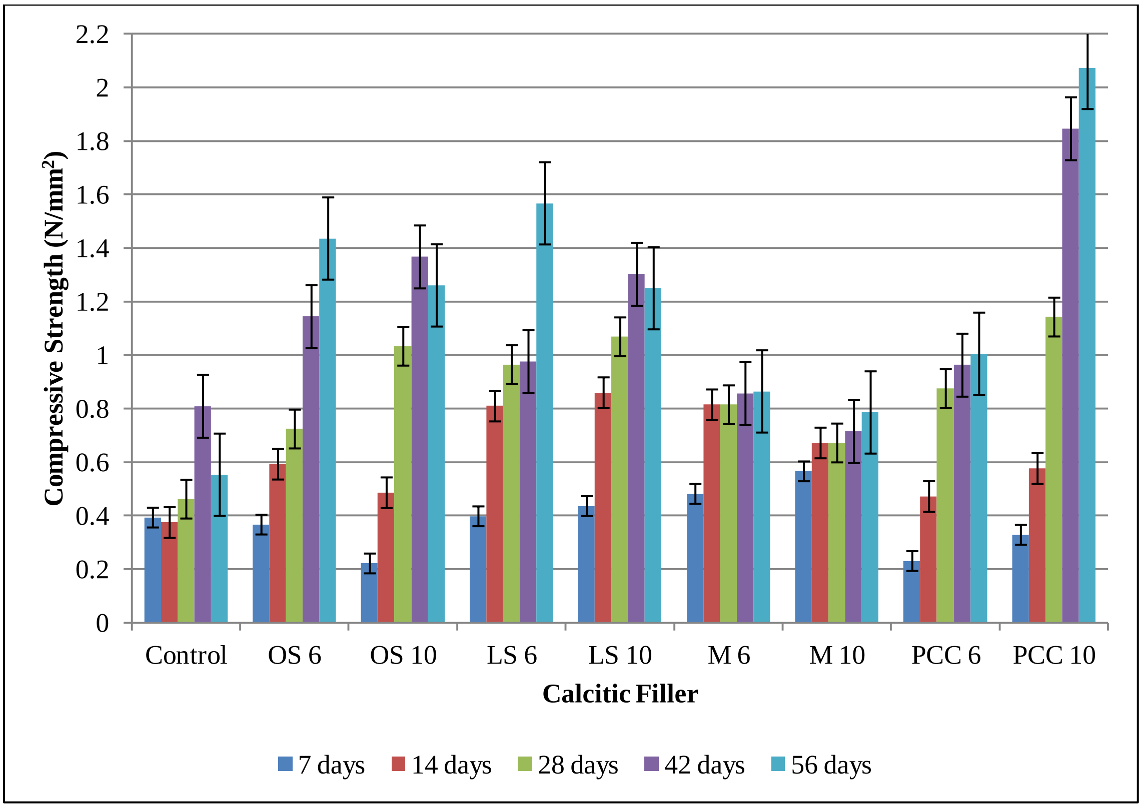


Figure 4.22: Compressive strengths at 33°C - 90% RH

4.8.4 Comparison of Compressive Strength between Mortars Based on Climates

The results obtained from the compressive strength test of lime mortars are presented in figure 4.20, 4.21 and 4.22. Experimental results indicate a clear difference between the seeded specimens and the control samples with regards to the development of compressive strength. It can be observed that, 27°C - 90% RH and 33°C - 90% RH modified specimens gained more strength than the standard 20°C - 60% RH condition.

4.8.5 Comparison of Compressive Strength between Mortars Based on Calcitic Fillers

Four types of calcitic fillers were used in this study; oyster shells powder, limestone powder, marble powder and precipitated calcium carbonate. Each type was subdivided into two amounts of seeding material, namely, 6% and 10%. From the data obtained, 100% of the total specimens in all climates with 10% of seeding recorded a higher compressive strength value than their 6% seeding amount counterpart.

The 10% limestone was further evaluated. In general, 10% limestone was associated with a significant difference compared to the control mortar. It gained 67% of compressive strength at 56 days compared to the early age of 7 days. At day 7, 33°C -

90% RH had the lowest value. Curing the mortar in the 20°C - 60% RH and 27°C - 90% RH climates gave comparative values, but 33°C - 90% RH was higher. An additional, evaluation was undertaken to determine the individual performance.

The 10% limestone in 20°C - 60% RH climate leads to a rapid early strength at day 14. This was followed by low development in the middle of the test duration and no strength loss up to the end of curing period. The 10% limestone in 27°C - 90% RH climate had a lower compressive strength compared to 10% limestone in 20°C - 60% RH but higher than 33°C - 90% RH.

The 10% limestone specimens cured in 27°C - 90% RH experienced 2% of strength loss after 42 days. The 10% of limestone seeding specimens cured in 33°C - 90% RH had the lowest compressive strength of all modified mortar. The 20°C - 60% RH and 33°C - 90% RH specimens did not undergo any strength loss at all time intervals.

The 10% precipitated calcium carbonate increased in strength. Specimens cured in 20°C - 60% RH gained strength rapidly and the highest strength attainment compared to other higher climates. That said, the specimens ultimately suffered a strength loss after 28 day. Specimens cured in 27°C - 90% RH showed slow strength development although they experienced a strength loss in the middle of the testing period. Specimens cured in 33°C - 90% RH had the lowest strength compared to other climates. However, the strength development showed that the relationship between strength and time in the 33°C - 90% RH was significant with no strength loss being noted until the end of the testing duration.

4.9 Sorptivity Analysis

Sorptivity is the mortar’s ability to absorb and transmit water through pores by capillary suction. In this experiment, the process was repeated 3 times to attain accuracy. The data obtained is shown according to respective climates. Sorptivity values were taken at 5 minute intervals for 30 minutes for each mortar sample. The volume of water absorbed (g/m^2) by capillarity at 5 minutes time intervals can be seen in Appendix C (Table C.1, C.2 and C.3).

These results were used to calculate the sorptivity coefficient, *k*. Based on Equation 3.3 in Section 3.8.1, the sorptivity coefficient, *k* (mm/min$^{0.5}$) was calculated by adopting the cross section of A= 1600mm^2. Figure 4.18, 4.19 and 4.20 show sorptivity coefficient, *k* of 20°C - 60% RH, 27°C - 90% RH and 33°C - 90% RH mortar specimens respectively. For data presentation, sorptivity coefficient, *k* values at 30 minutes (final readings) were taken.

Figure 4.23, 4.24 and 4.25 show the water absorption depth, *i* (mm) at 56 days against the square root of submerged time (min$^{0.5}$). If equation 3.3 is valid, the graphs should generate a straight line and the capillarity coefficient and sorptivity will be the gradient of the straight line. This is true for all specimens in all climates with exception of the mortars modified with precipitated calcium carbonate 6% cured in 33°C - 90% RH condition.

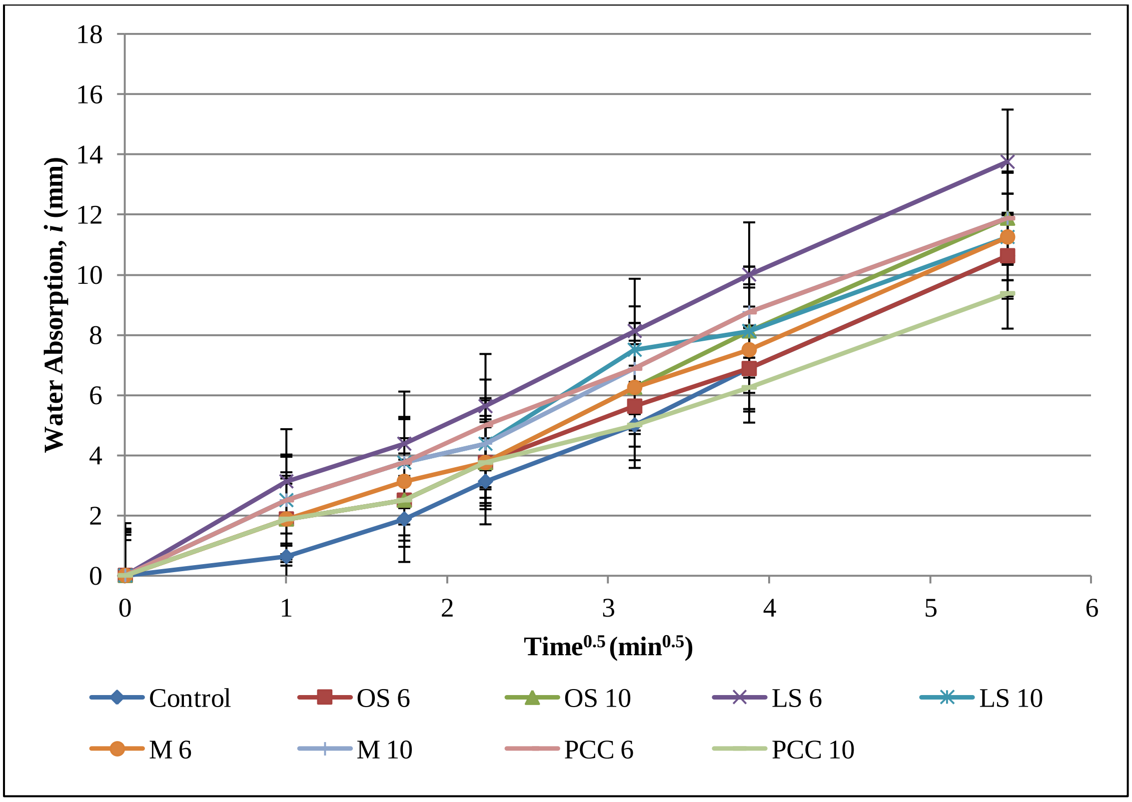


Figure 4.23: Water Absorption at 20°C - 60% RH

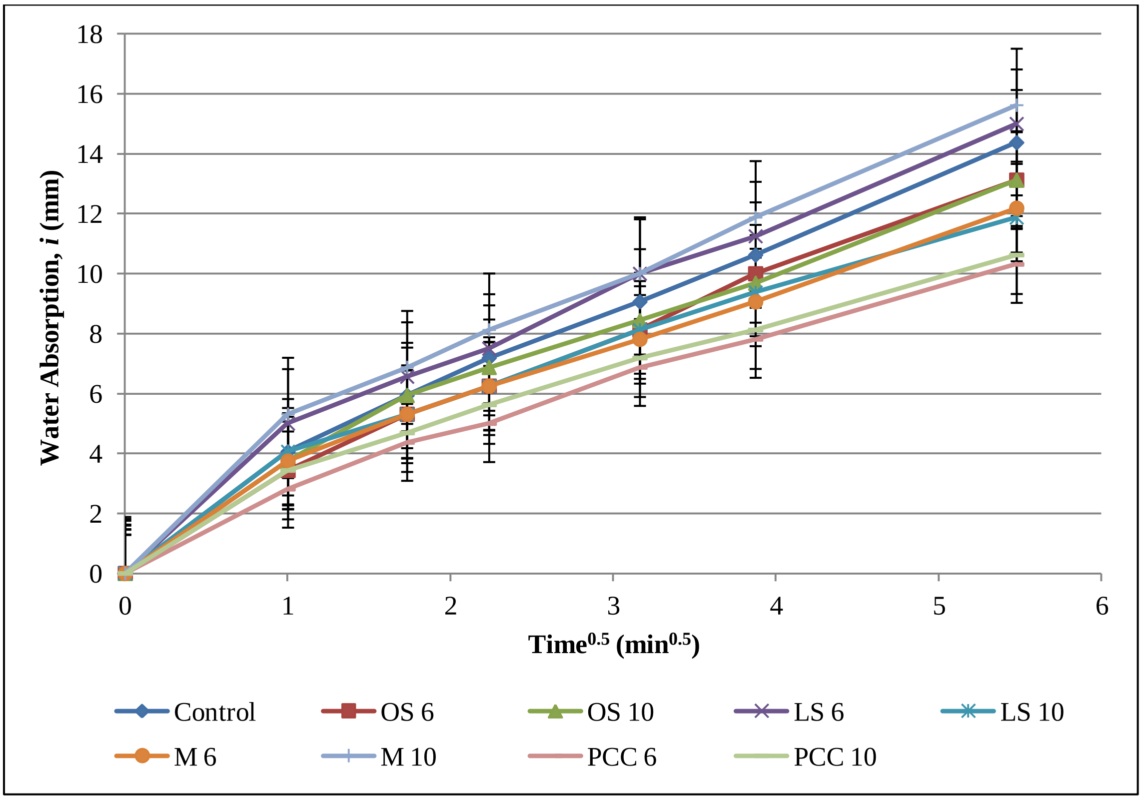


Figure 4.24: Water Absorption at 27°C - 90% RH

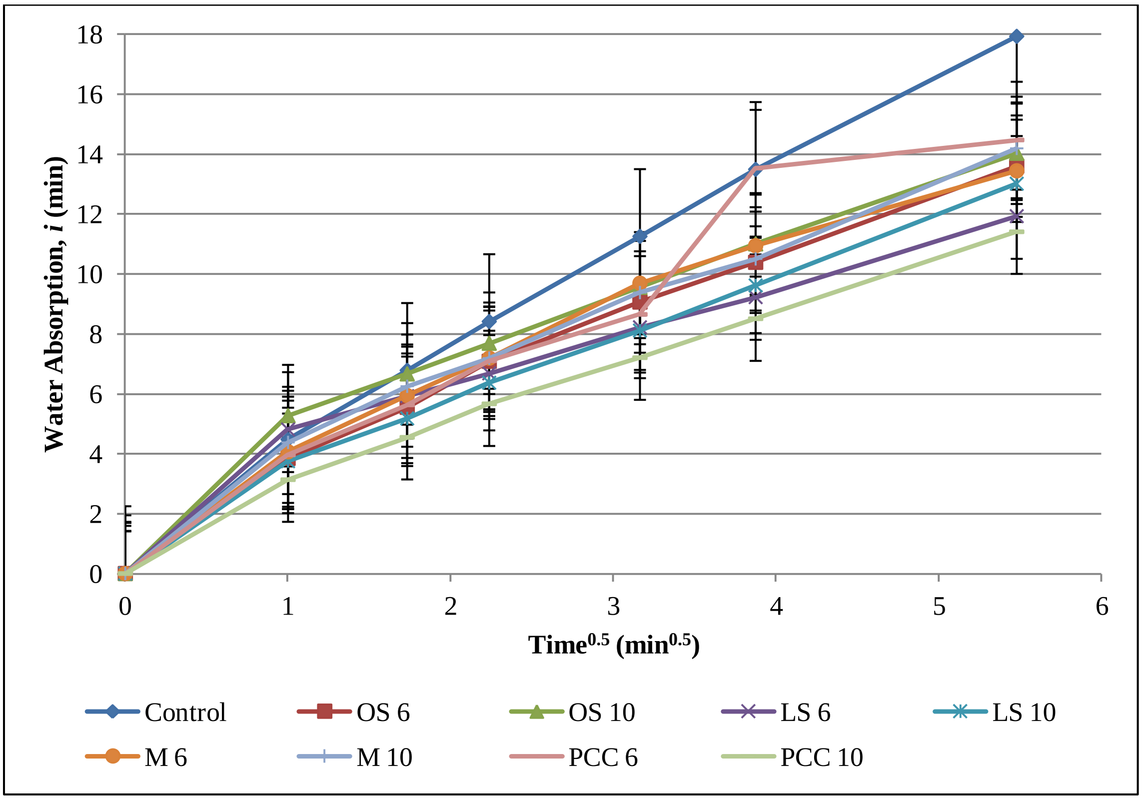


Figure 4.25: Water Absorption at 33°C - 90% RH

Figure 4.26, 4.27 and 4.28 provide sorptivity coefficient, *k* at 20°C - 60% RH, 27°C - 90% RH and 33°C - 90% RH respectively. There is a slight difference in the water absorption rates of the different specimens tested. From the figure, there were inconclusive patterns on water absorption.

4.9.1 Sorptivity Coefficient, k at 20°C - 60% RH

It is apparent from Figure 4.26 that there is not a significant difference in the *k* values between the formulations. The sorptivity coefficient values of all mortars vary from 1.5 – 3mm/min$^{0.5}$. For the first 28 days, the control mortars generally exhibited increased absorption of water over other samples, surpassing the other modified mortars (although there are some exceptions). However, the values decreased after 28 days until the end of the curing period. The most striking result to emerge from the data was that the sorptivity coefficient values of the control mortars at day 7 and day 56 was comparable (3% difference).

The highest sorptivity coefficient was 6% limestone. Conversely, the lowest sorptivity coefficient was 10% precipitated calcium carbonate. At the end of the curing period (56 days), only 6% (OS 6) oyster shell and 10% (PCC 10) precipitated calcium carbonate have the lower sorptivity coefficients than the control specimens.

4.9.2 Sorptivity Coefficient, k at 27°C - 90% RH

Figure 4.27 compares the sorptivity coefficient, *k* of each mortar formulations at 27°C - 90% RH. In general, the sorptivity coefficient values of all mortars vary from 1.5 – 4mm/min$^{0.5}$ in which sorptivity coefficient values of modified mortars vary from 1.5 – 3mm/min$^{0.5}$. All modified mortars have lower sorptivity coefficient values throughout the testing period although there are some exceptions at day 56. At day 7, control mortars had the highest sorptivity coefficient (3.8mm/min$^{0.5}$). However, the value dropped to 2.95mm/min$^{0.5}$ at day 14. Precipitated calcium carbonate 10% (PCC 10) has the lowest sorptivity coefficient values compared to other mortars. It is apparent from these results that modified mortars with calcitic fillers produced denser pore structure than un-modified mortars.

4.9.3 Sorptivity Coefficient (k), at 33°C - 90% RH

Figure 4.28 presents the sorptivity coefficient *(k),* of all mortars cured in 33°C - 90% RH climate. Generally, the sorptivity coefficient values of all mortars vary from 1 – 4mm/min$^{0.5}$ in which sorptivity coefficient values of modified mortars vary from 1 –

3.2mm/min$^{0.5}$. All modified mortars had lower sorptivity coefficient values throughout the testing period although 10% marble (M 10) at days 14 was an exception.

The sorptivity coefficient of control mortars increased from day 7 but subsequently the values dropped by 5.7% after 42 days of curing. The values then further dropped by another 5.7% at the end of curing period. The most striking result to emerge from the data is that the sorptivity coefficient values of controlled mortars at day 7 and day 56 was comparable (5.6% difference).

6% limestone (LS 6) had the lowest sorptivity coefficient values compared to other mortars. This was followed by precipitated calcium carbonate 10% (PCC 10). It is apparent from these results that modified mortars with calcitic fillers produced a denser pore structure than un-modified mortars. Further statistical tests revealed due to the large standard error bar in 6% oyster shells (OS 6), the day 7 sorptivity coefficient value of k= 1.03mm/min$^{0.5}$ could be disregarded.

4.9.4 Overall Observation

The values of sorptivity coefficients were observed up to the end of tests (56 days). Figure 4.26, 4.27 and 4.28 show that the control mortars generally exhibited an increased absorption of water over other samples, although there are some exceptions. Overall the sorptivity coefficient values of all mortars cured in all climates vary from 1 – 4 mm/min$^{0.5}$. Further analysis showed that modified mortars have a lower sorptivity coefficient values compared to non-modified mortars although there are some exceptions in 20°C - 60% RH. The most significant difference between un-modified with modified mortar performance can be seen in 33°C - 90% RH. It can be concluded that mortar modifications with calcitic filler generally reduce the sorptivity for mortars cured in high temperature and humidity environments.

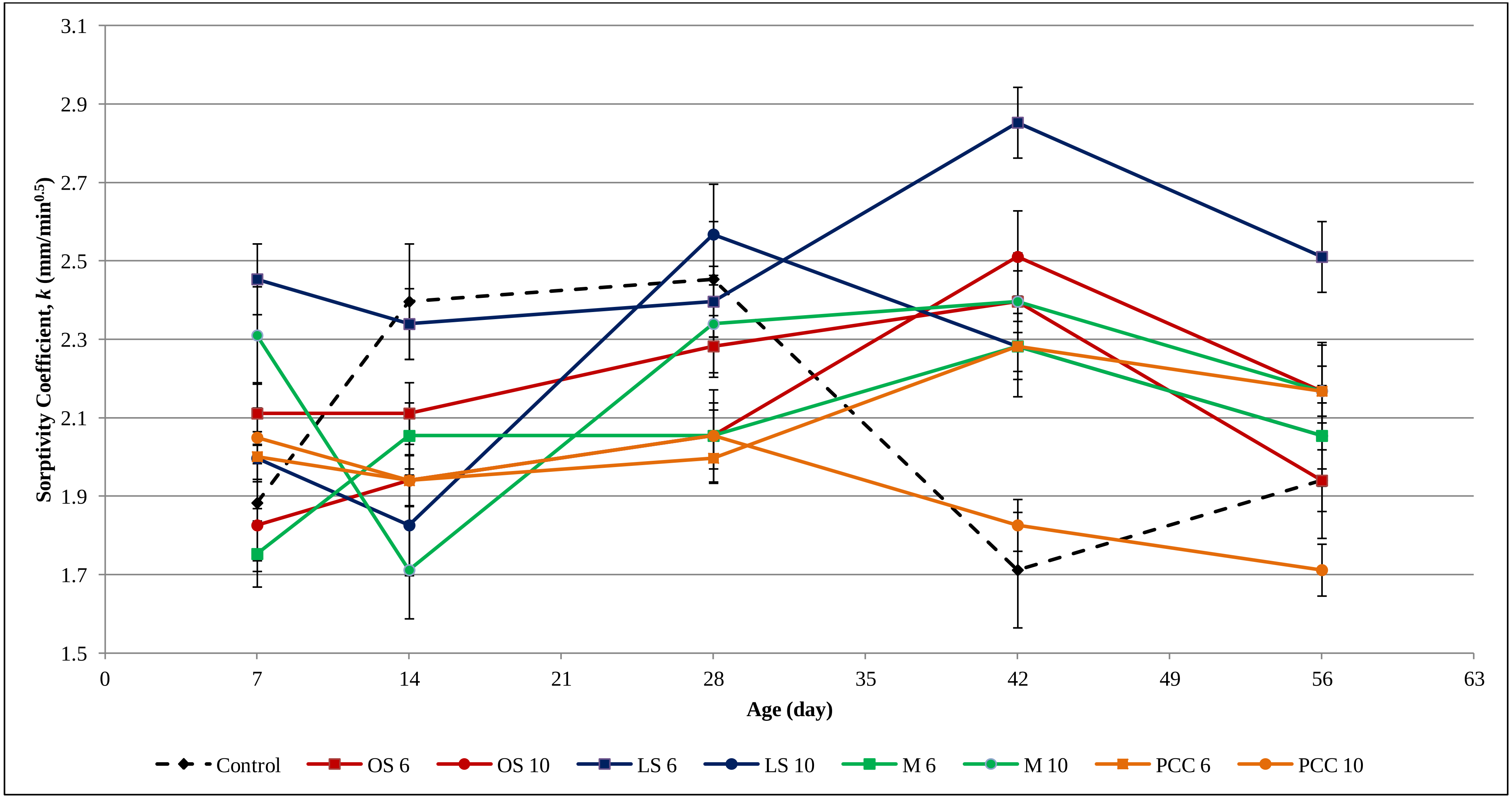


Figure 4.26: Sorptivity coefficient (*k*), at 20°C - 60% RH

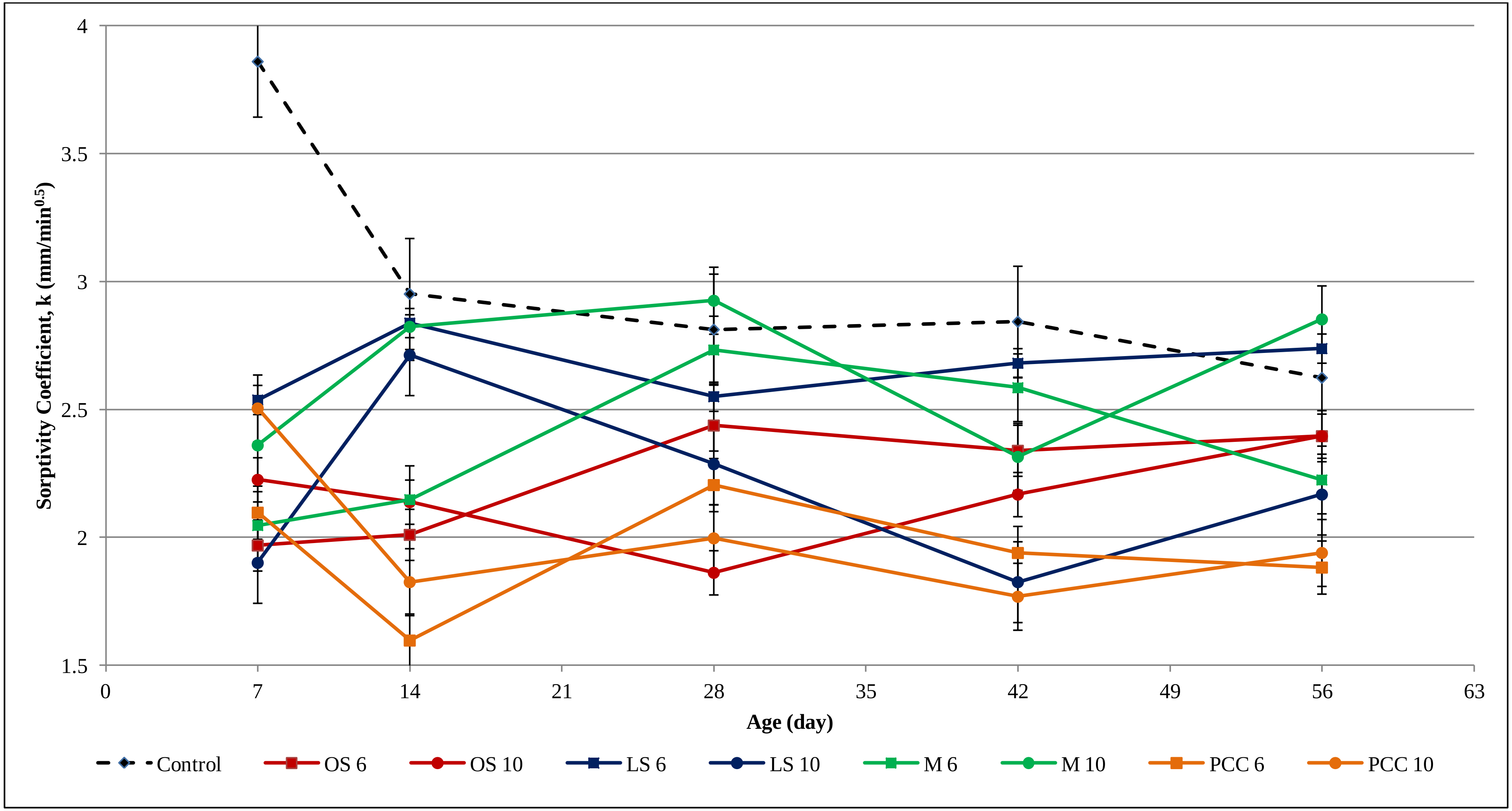


Figure 4.27: Sorptivity coefficient (*k*), at 27°C - 90% RH

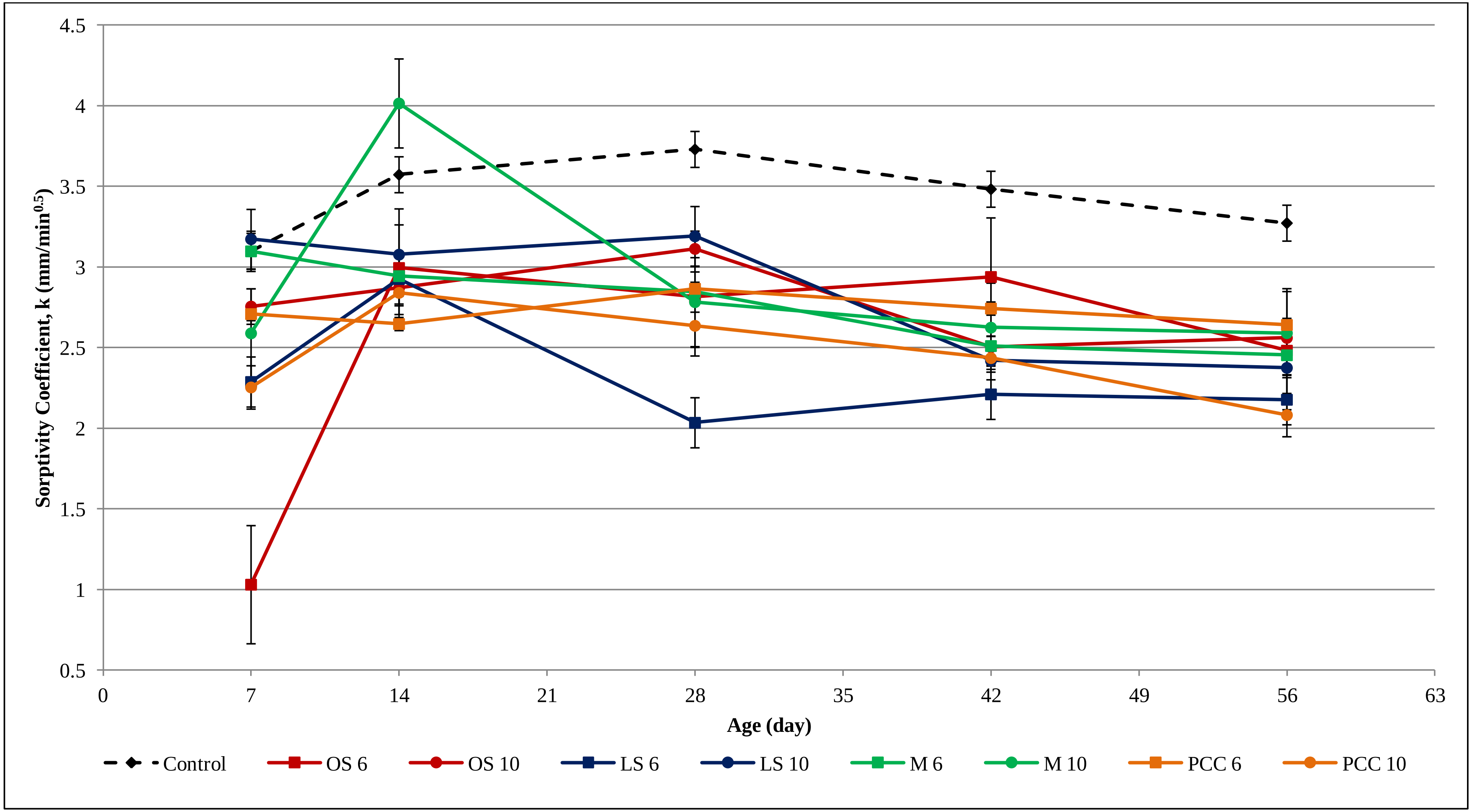


Figure 4.28: Sorptivity coefficient (*k*), at 33°C - 90% RH

4.10 Microscopy Analysis by Scanning Electron Microscopy (SEM)

ESEM analysis was undertaken upon a representative proportion of specimens formerly utilized for chemical and physical characteristics experiments. These had been kept in vacuum sealed sample bag to avoid any contamination or continuation of carbonation. Carbon coating was used as the standard method for preparing non-conducting or poorly conducting specimens for observation in SEM.

Lawrence (2006) adopted 500x magnification as it was representative of traditional approaches for deriving the significant information on surface characteristics (Wong et al, (2006). However, due to complexity of the pore structure development of the lime mortars a, larger magnification (1500x) has been adopted to identify calcite crystalline formations. The full set of ESEM images can be seen in Appendix B: Environmental Scanning Electron Microscopy (SEM) Images of Lime Mortars.

Even though there are significant differences in mortar's strength based on the amount of substitution, there are no significant differences in surface textures identified by microscopy. In this section, only 10% seeding formulations are discussed. This was due to 88% of compressive strength results showing that seeding mortars with 10% is more effective than 6%.

4.10.1 Calcitic Fillers

Calcitic fillers of oyster shells, limestone and marble have been analyzed for ESEM imaging. All calcite fillers exhibited a large proportion of calcite crystals especially oyster shells and limestone. Figure 4.29 to 4.34 illustrate the microscopy images of the calcite fillers at 10µm and 200µm.

4.10.2 Oyster shells

Scanning electron micrographs (SEM) of the surface structures of oyster shells subjected to different magnifications are presented in Figure 4.29 and 4.30. The rough surface has moderately sculptured textural form. From Figure 4.29, there is presence of aragonite flower-like polycrystalline structures in between the calcite crystals. Conventionally, the aragonite polymorph of $CaCO_3$ possesses a 'needle-like' morphology.

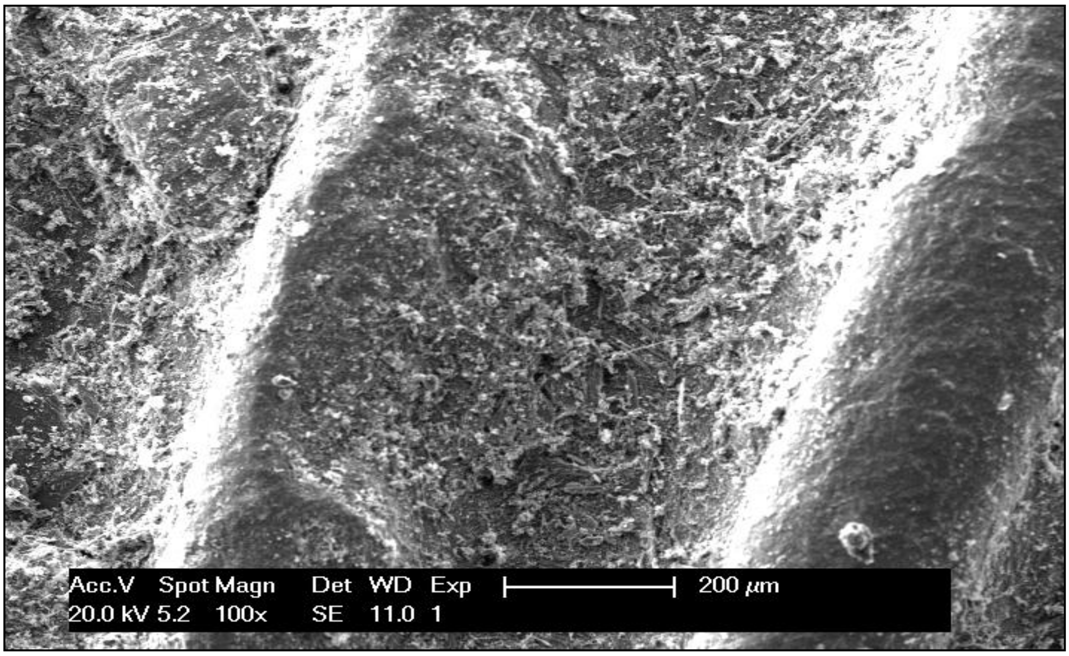


Figure 4.29: SEM image of oyster shells at 200µm

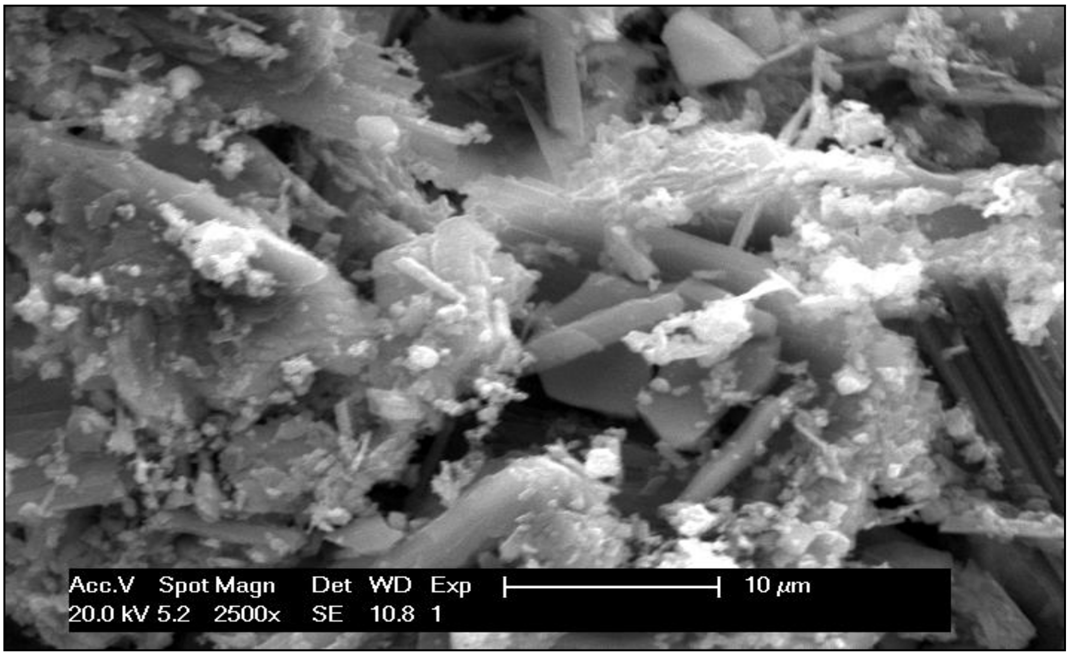


Figure 4.30: SEM image of oyster shells at 10µm

4.10.3 Limestone

The limestone specimen has a rough and uneven surface. At 100x magnification (see Figure 4.31), the wide array of pore sizes in limestone is illustrated. Large cylindrical pores in the order of 2µm are noticeable across the sample (see fig. 4.32). Many other pore geometries are also observed.

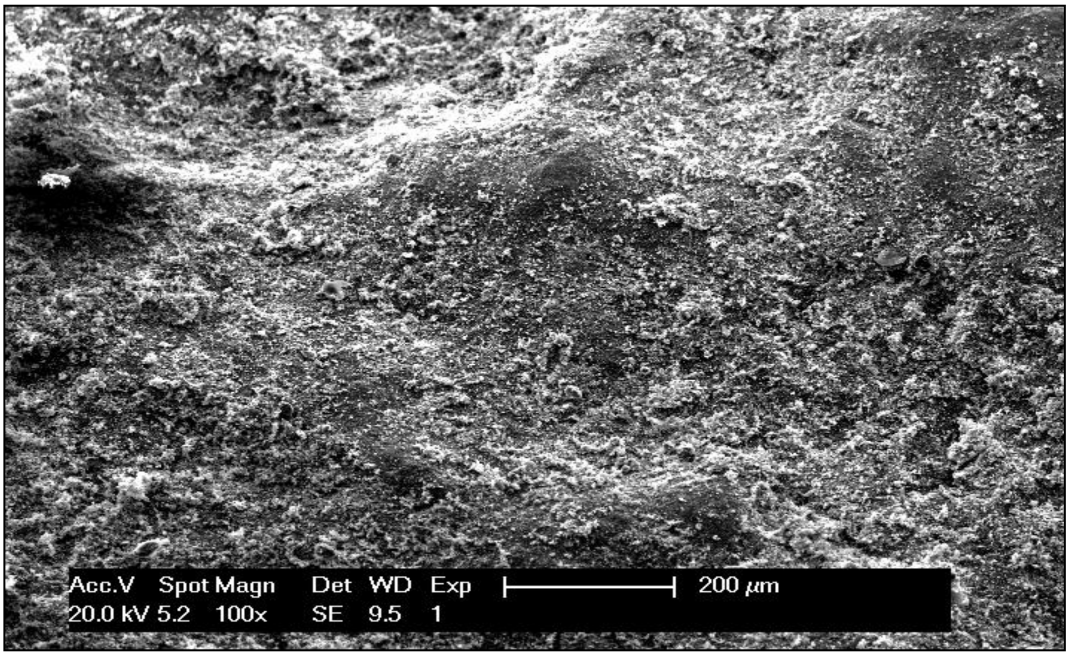


Figure 4.31: SEM image of limestone at 200µm

From the Figure 4.32 below, limestone's calcite crystalline formations are seen to be rhombohedral, with the interspersed cauliflower-like structures. These dense formations are scattered and unevenly distributed. The dark regions denote pore structure that is approximately 1-2µm. The mortar appears relatively porous with great pore interconnectivity. As the magnification increases, it becomes apparent that most of these seemingly large pores are actually comprised of many micro pores.

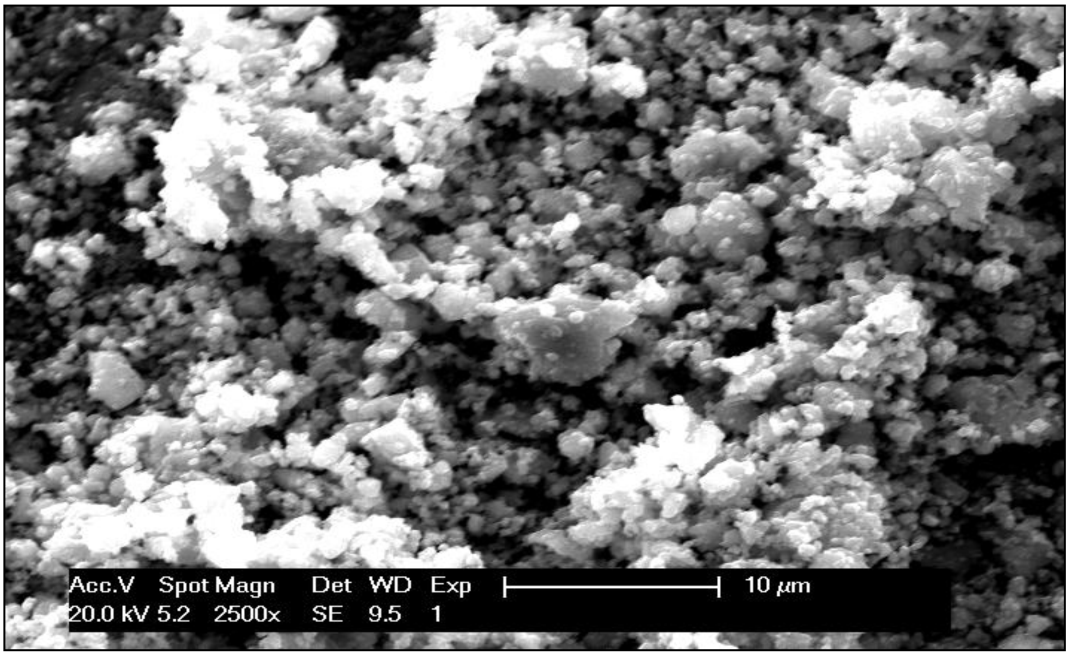


Figure 4.32: SEM image of limestone at 10µm

4.10.4 Marble

The marble specimens are hard and therefore not easily broken. Fig. 4.33 indicates a relatively flat surface (see Figure 4.33). Dolomite micro crystals in this marble specimen occur as plates and fine particles. Marble is shown to have a small number of calcite crystalline formations as shown in Figure 4.34.

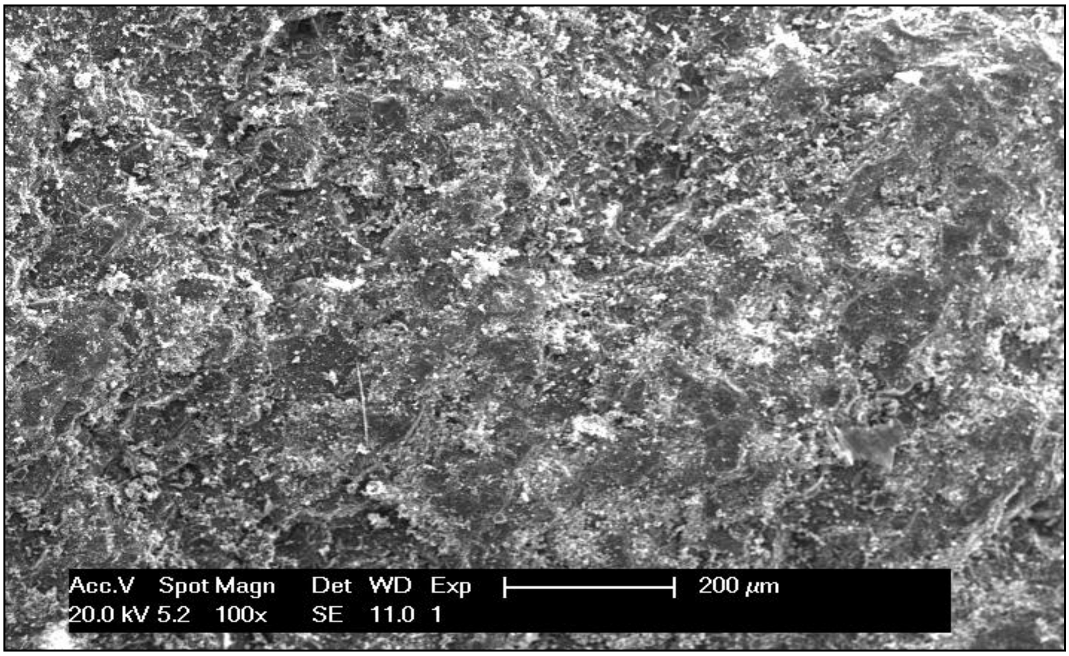


Figure 4.33: SEM image of marble at 200µm

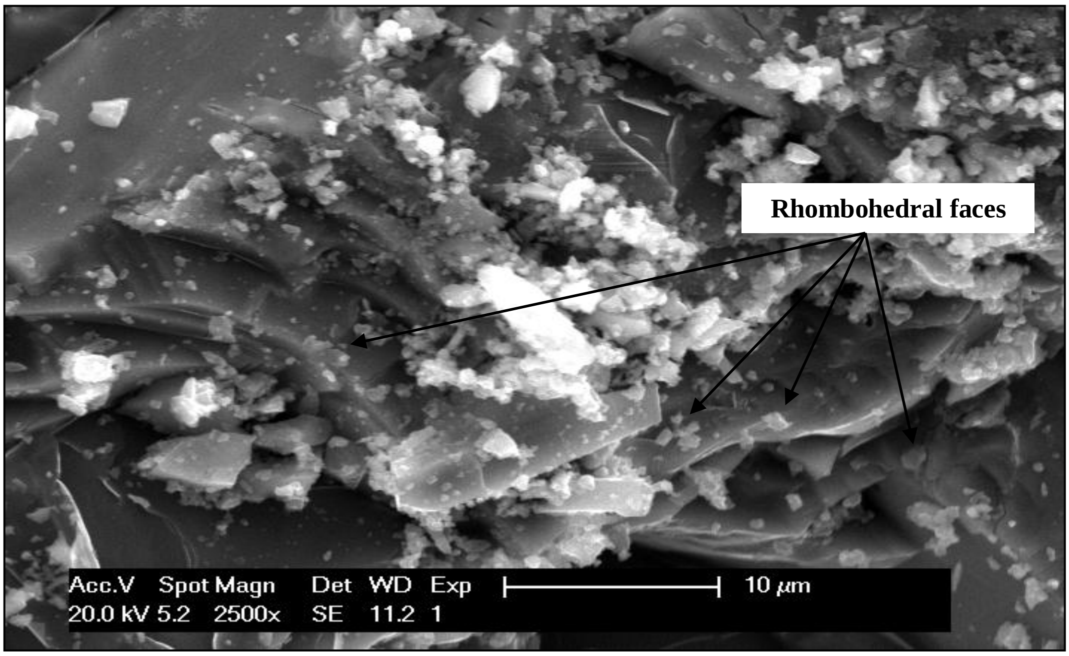


Figure 4.34: SEM image of marble at 10µm

Rods, plates, and fine particles associated with calcite from the marble are specifically shown in Figure 4.34. The ratio of plate width to plate thickness varies greatly (hence not all of the dolomite plates represent the equilibrium shape). The ends of the plates appear to exhibit rhombohedral faces.

4.10.5 Calcitic Filler Modification Effects on Microscopy Development in Control Climate of 20°C - 60% RH

Figure 4.35, 4.36, 4.37, 4.38, 4.39, 4.40, 4.41 and 4.42 illustrate the modified lime mortar pore development cured in 20°C - 60% RH condition. At day 7, images revealed visible pores (black pixel or darker region). Overall, the crystalline formation appears irregular in trigonal-rhombohedral shapes and sizes. Individual calcite crystal surface appeared to be uneven; with smooth interspersed, interlocking blocks occurring.

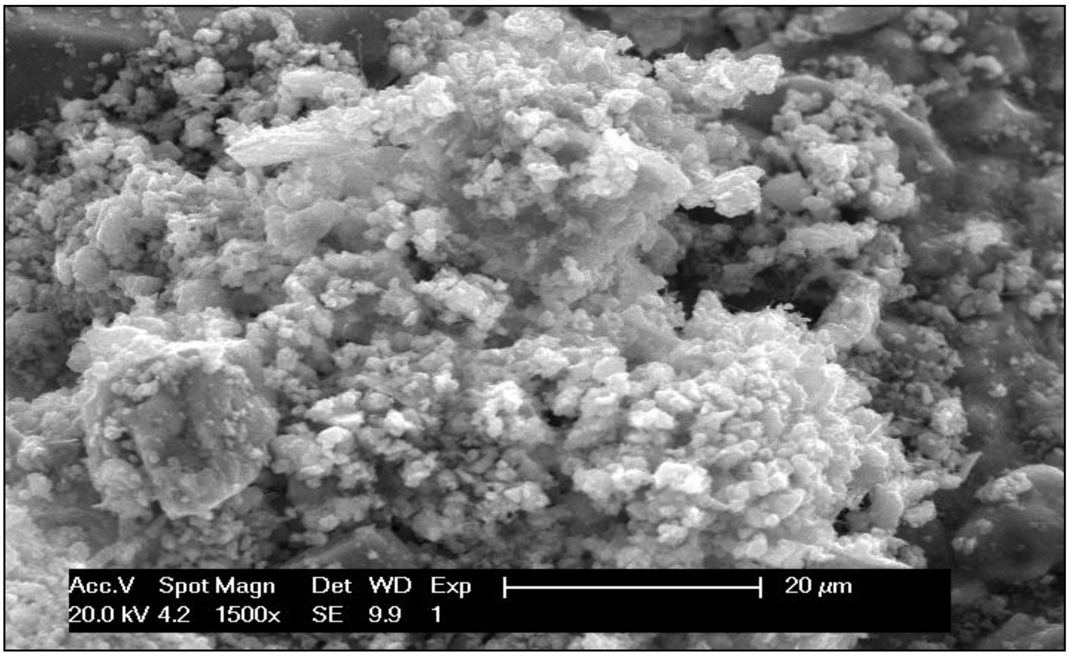


Figure 4.35: SEM image of mortar with 10% oyster shells at 7 days (20-60)

Figure 4.35 shows the formation of multi-layered primary hydration products of C-S-H. The oyster shells distribution in irregular shapes is difficult to identify due to the oyster shells relative small proportion. As shown in Figure 4.36, limestone mortar exhibited the crystalline formation of calcite rhombohedral with visible needlelike mortar hydration products being interspersed. This is a typical morphology associated with ettringite phases. However this cannot be confirmed without further investigation. Modified mortar with marble (see Figure 4.37) also exhibited the crystalline formation of rhombohedral calcite with visible needlelike products of hydration being interspersed.

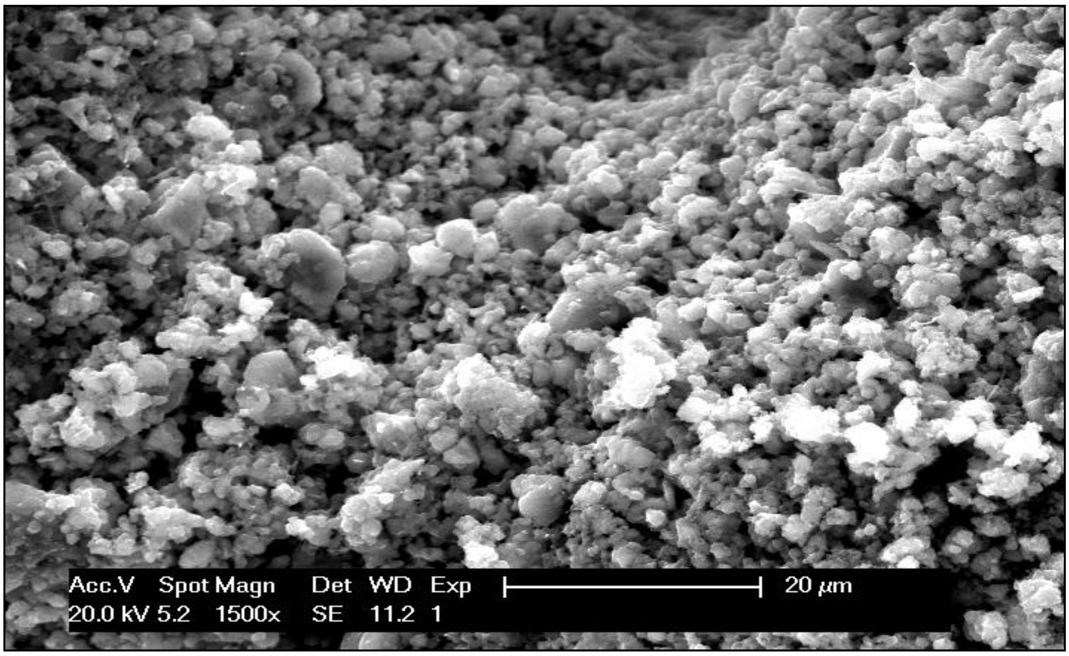


Figure 4.36: SEM image of mortar with 10% limestone at 7 days (20-60)

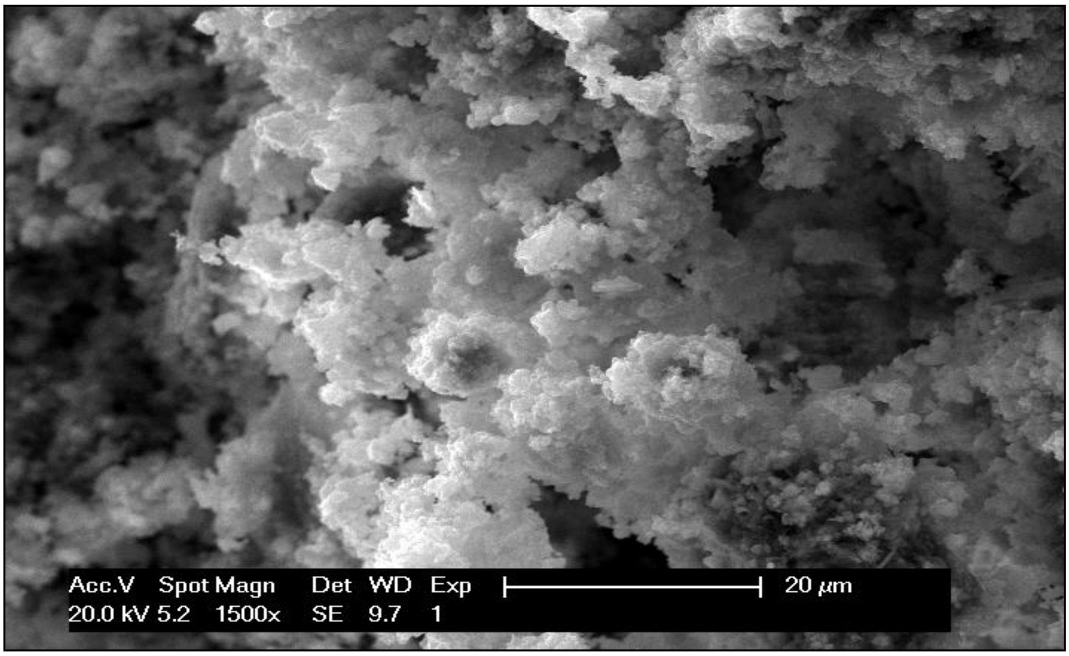


Figure 4.37: SEM image of mortar with 10% marble at 7 days (20-60)

Precipitated $CaCO_3$ specimens were observed to form the biggest calcite crystals relative to the other specimens (Figure 4.38). It is believed that large calcite crystals produce a stronger mortar. This is consistent with strength results stating that precipitated $CaCO_3$ specimens yielded the best strength development of all mortars.

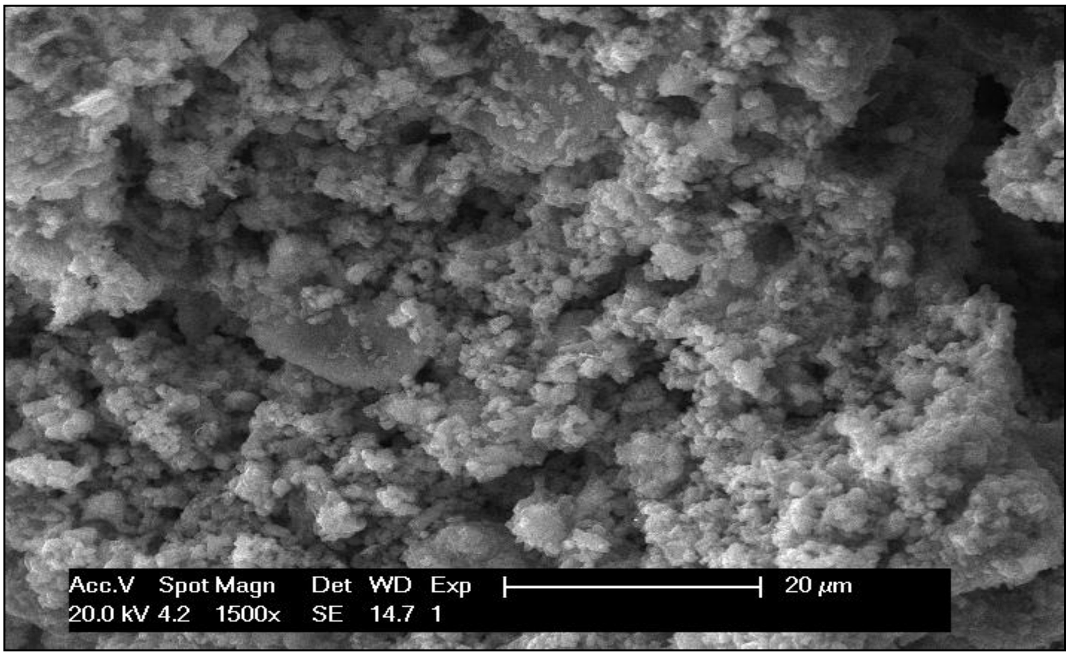


Figure 4.38: SEM image of mortar with 10% precipitated $CaCO_3$ at 7 days (20-60)

Towards the end of testing period (56 days), visible calcite hexagonal prism crystals and products of hydration can be identified. Oyster shells are observed to have a significant amount of needle-like crystal of ettringite (see Figure 4.39). Limestone formed multi-layered petal-like shaped calcite pallets (Figure 4.40).

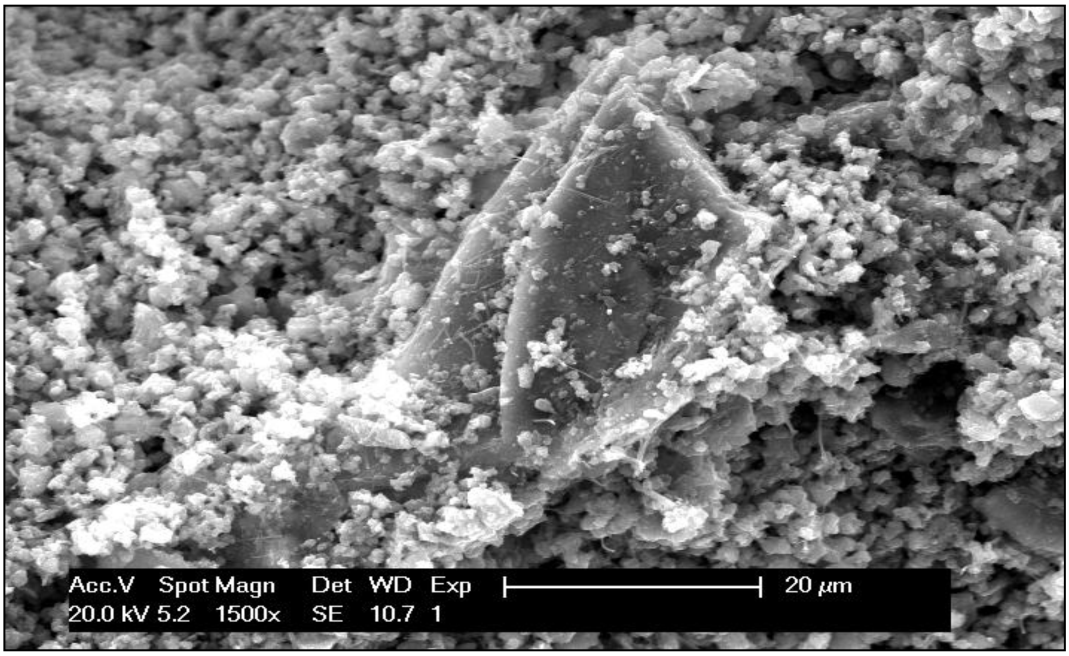


Figure 4.39: SEM image of mortar with 10% oyster shells at 56 days (20-60)

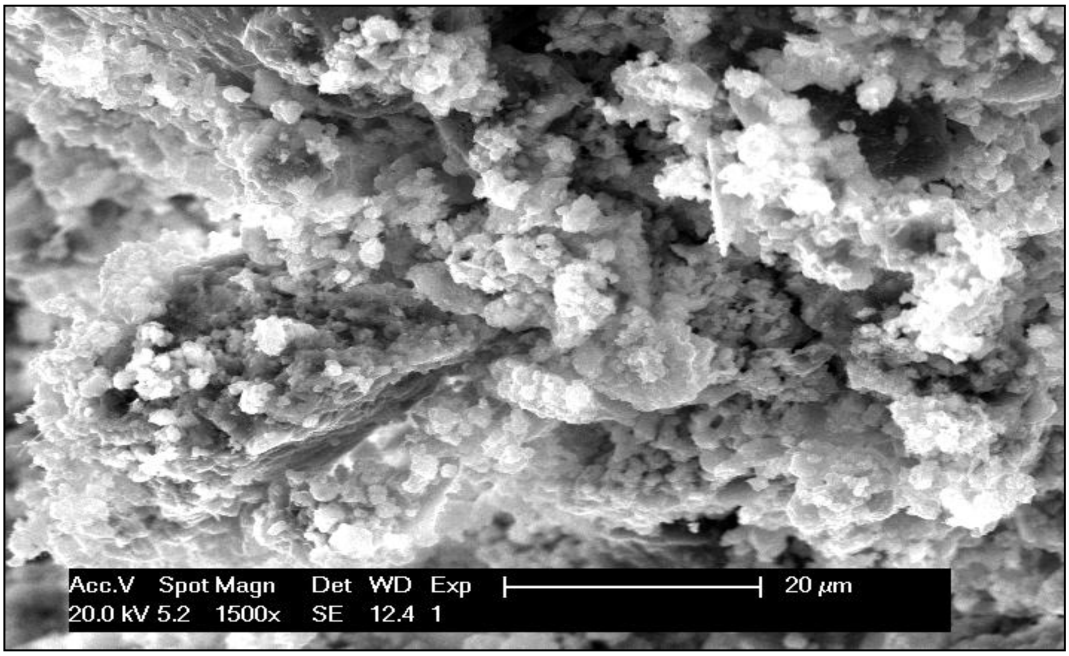


Figure 4.40: SEM image of mortar with 10% limestone at 56 days (20-60)

Figure 4.41 indicates dispersed hexagonal calcite prisms in marble mortar. It does not have a readily identifiable form. The porous structures were mostly granulated and the porosity was significantly enhanced. Visible rhombohedral calcite is visible in the precipitated $CaCO_3$ mortars (Figure 4.42) although in contrast, the mortar shows considerable areas of aggregate without any calcite crystals attached to the surface.

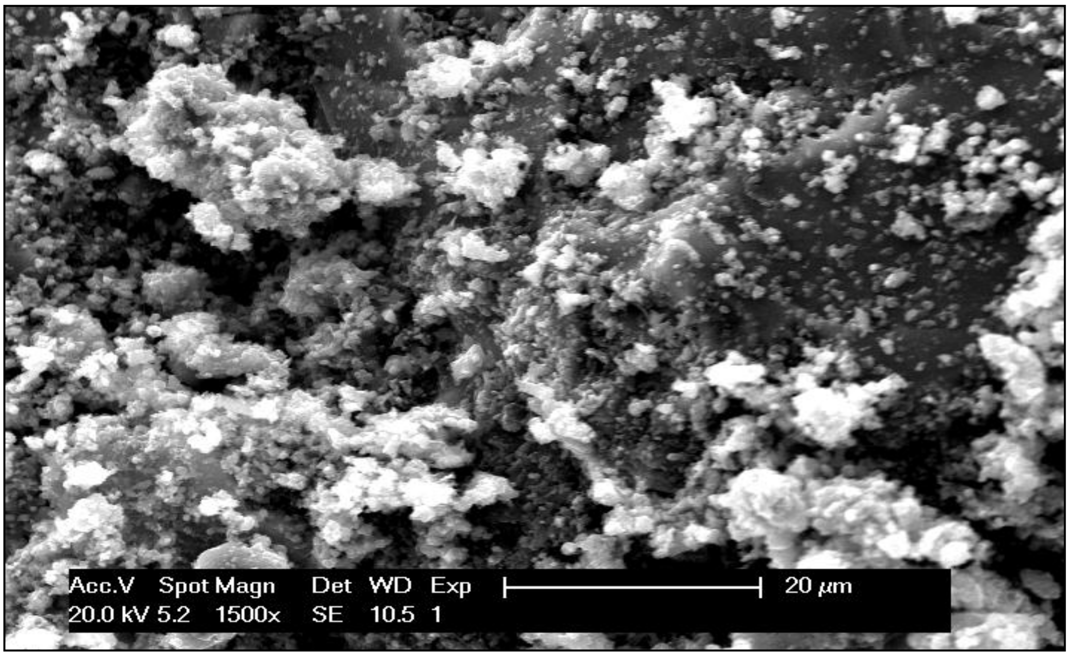


Figure 4.41: SEM image of mortar with 10% marble at 56 days (20-60)

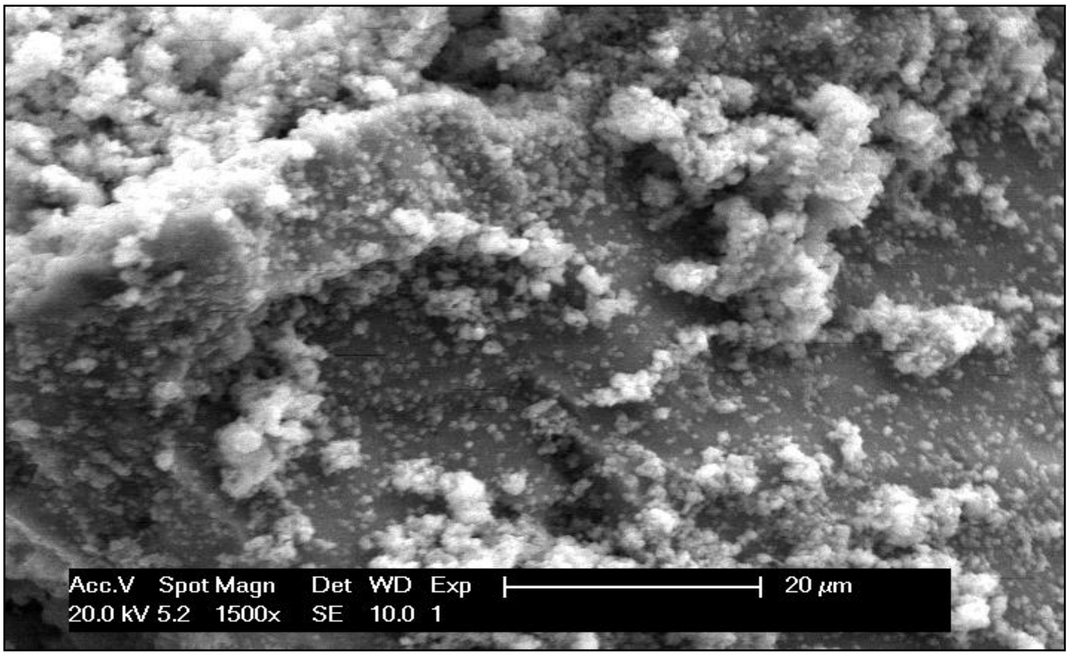


Figure 4.42: SEM image of mortar with 10% precipitated $CaCO_3$ at 56 days (20-60)

4.10.6 Calcitic Filler Modification Effects on Microscopy Development in 27°C - 90% RH

Figure 4.43, 4.44, 4.45, 4.46, 4.47, 4.48, 4.49 and 4.50 illustrate the modified lime mortar pore development cured in 27°C - 90% RH condition. Morphological observations revealed featureless formations and irregular shapes and sizes of calcite can be identified as early as day 7. At day 7, modified mortars (see Figure 4.43, 4.44, 4.45, 4.46) show a dense crystal formation compared to seeded mortars cured in 27°C - 60% RH condition. However, a visible formation of possible ettringite can be identified. However this cannot be confirmed without further investigation. Limestone mortar (see Figure 4.44) showed a granulated structure with visible pores (black pixel or darker region).

In Figure 4.46, mortar with precipitated calcium carbonate showed calcite formed as large rhombohedral shape. The overall crystalline formation appears irregular in trigonal-rhombohedral shapes and sizes. Individual calcite crystal surfaces appeared to be uneven; with smooth inter dispersed blocks.

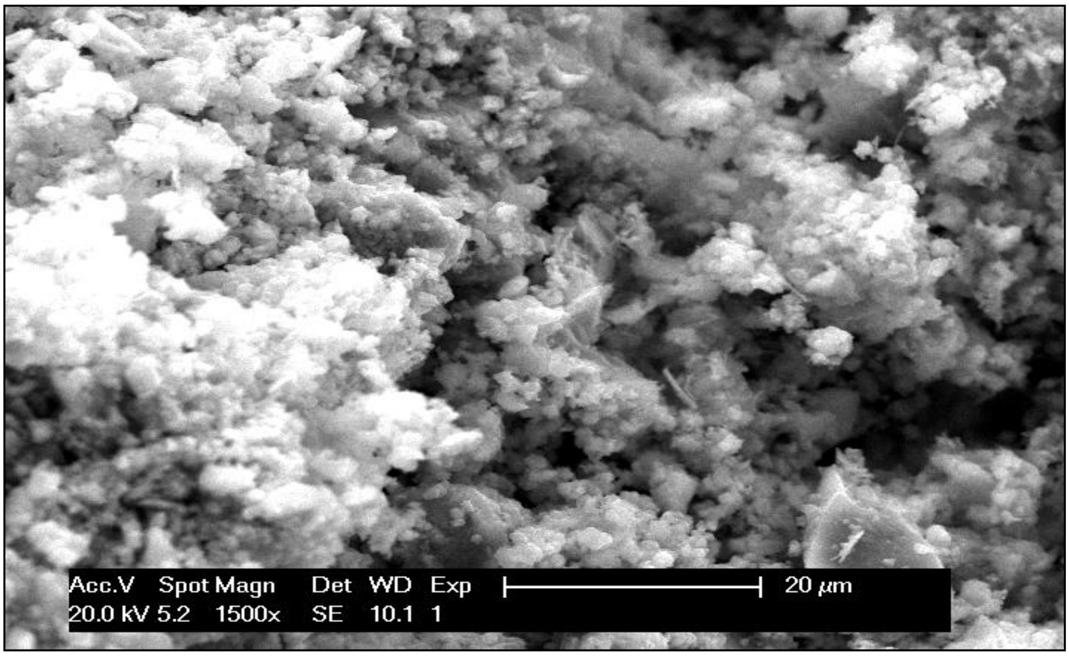


Figure 4.43: SEM image of mortar with 10% oyster shells at 7 days (27-90)

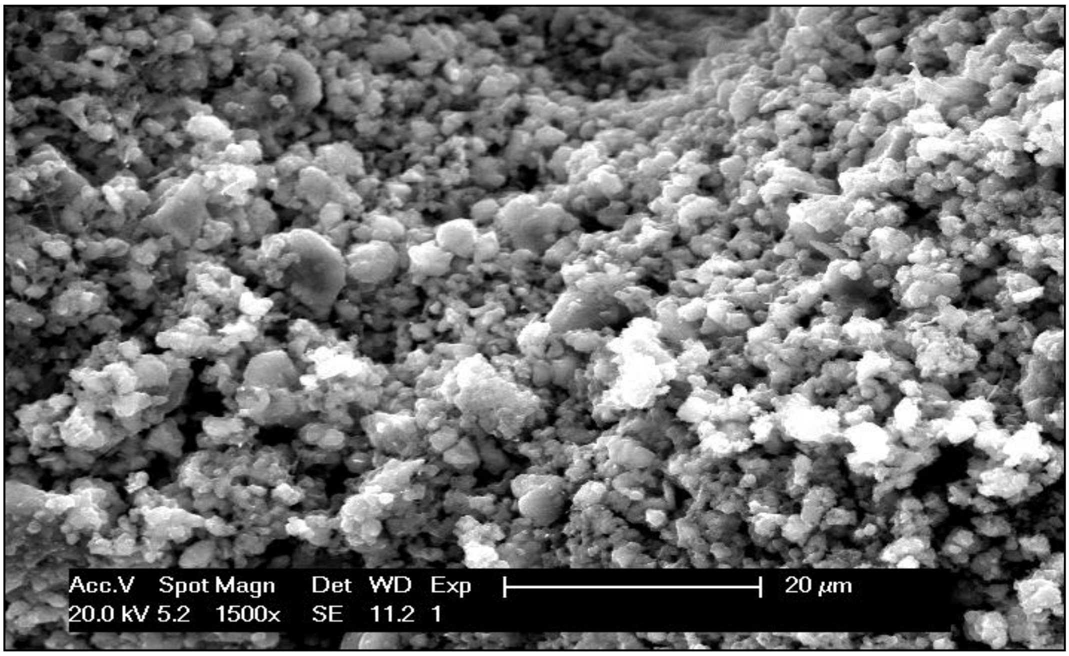


Figure 4.44: SEM image of mortar with 10% limestone at 7 days (27-90)

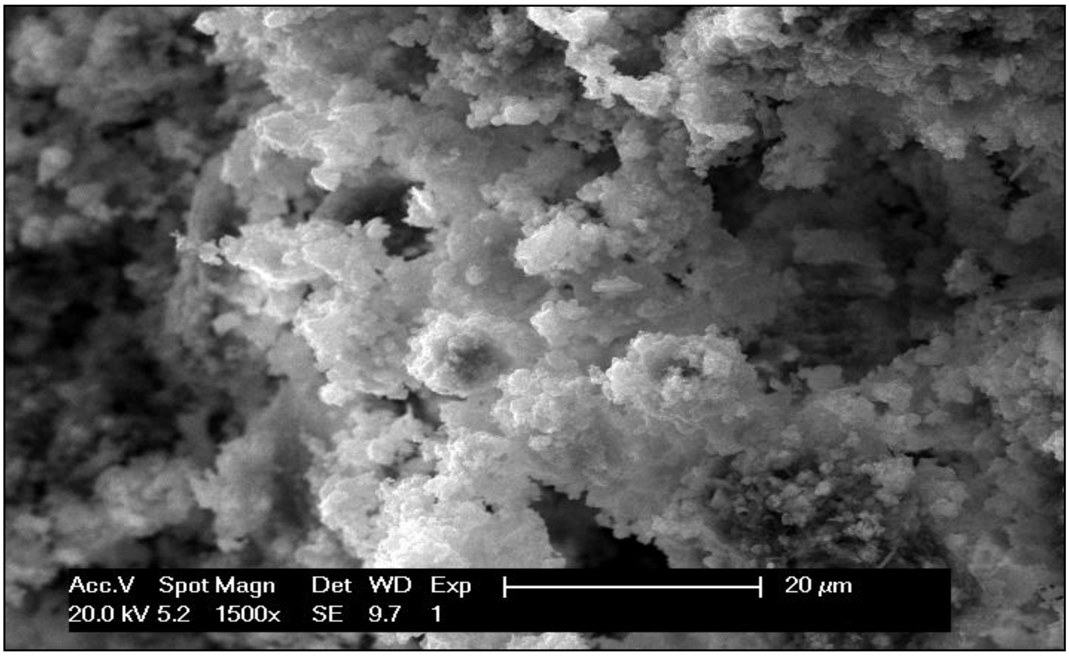


Figure 4.45: SEM image of mortar with 10% marble at 7 days (27-90)

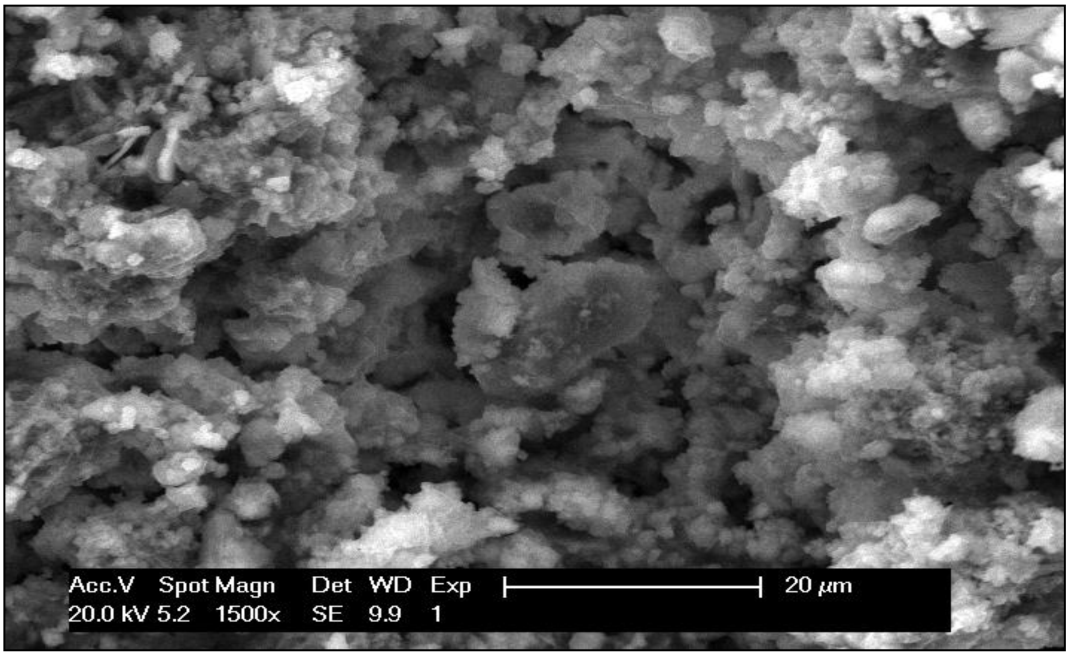


Figure 4.46: SEM image of mortar with 10% precipitated $CaCO_3$ at 7 days (27-90)

Figure 4.47, 4.48, 4.49 and 4.50 show the SEM images of modified mortars at day 56 of testing. At 56 days, modified mortars exhibit a microstructure resembling an epitaxial growth pattern, which consists of cubic and needle-like crystals. Mortar with oyster shells (see Figure 4.47) formed multi-layered petal-like shape of calcite. Towards the end of testing period of the mortar with inclusions of the limestone, marble and precipitated $CaCO_3$ (see Figure 4.48, 4.49 and 4.50), showed signs of visible hexagon prism development of calcite from the hydration process. Additionally, there is a smaller amount of interlocking crystals at a constant angle and direction forming the basic framework.

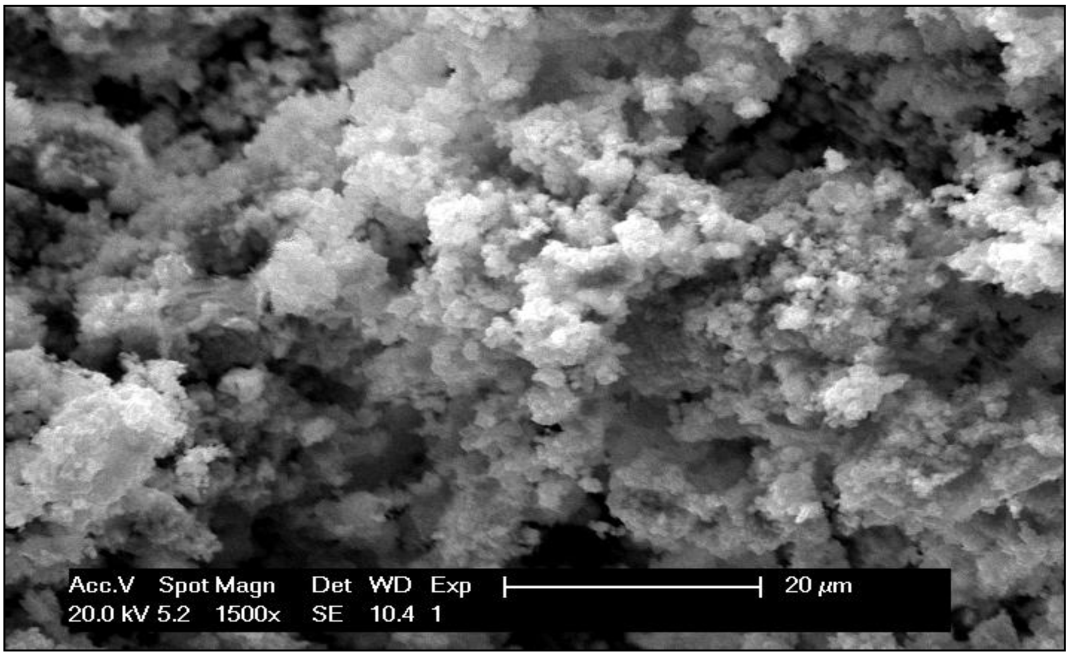


Figure 4.47: SEM image of mortar with 10% oyster shells at 56 days (27-90)

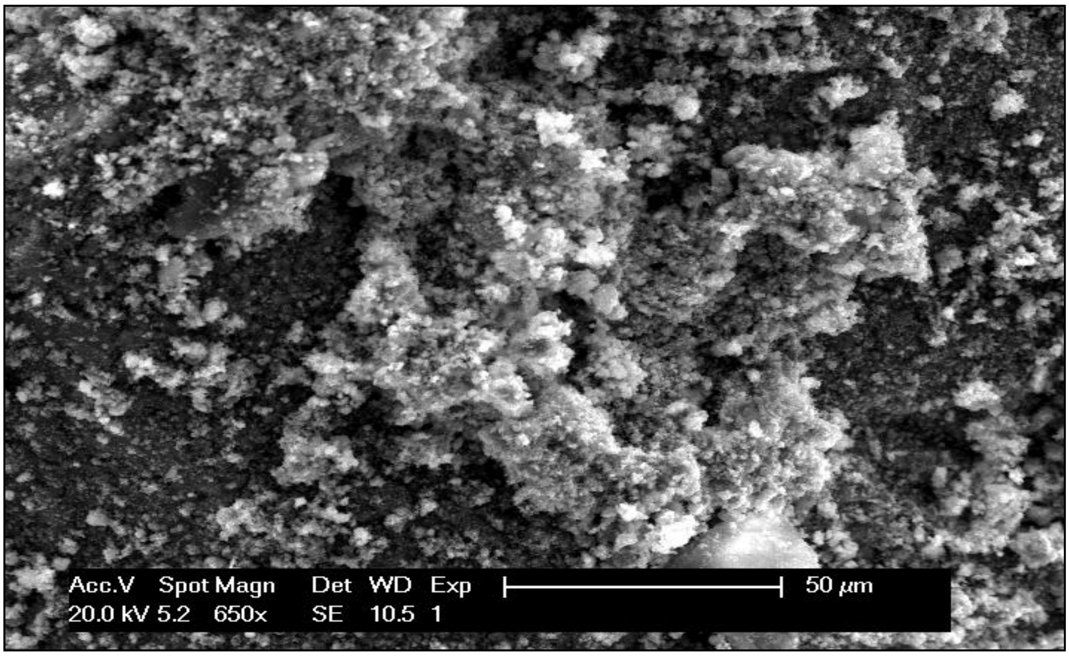


Figure 4.48: SEM image of mortar with 10% limestone at 56 days (27-90)

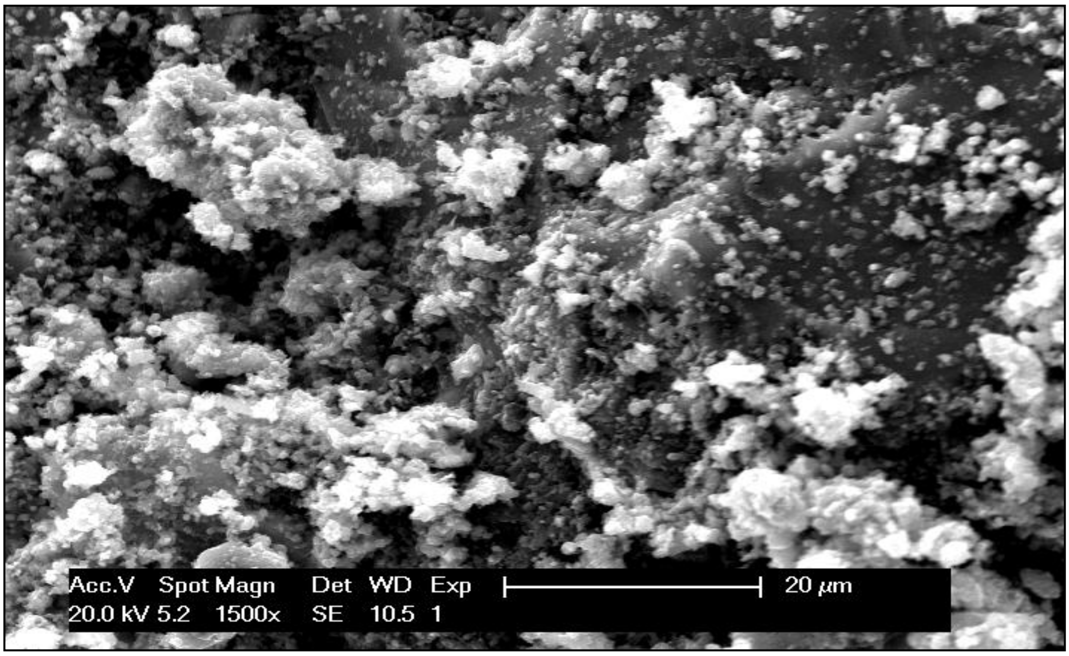


Figure 4.49: SEM image of mortar with 10% marble at 56 days (27-90)

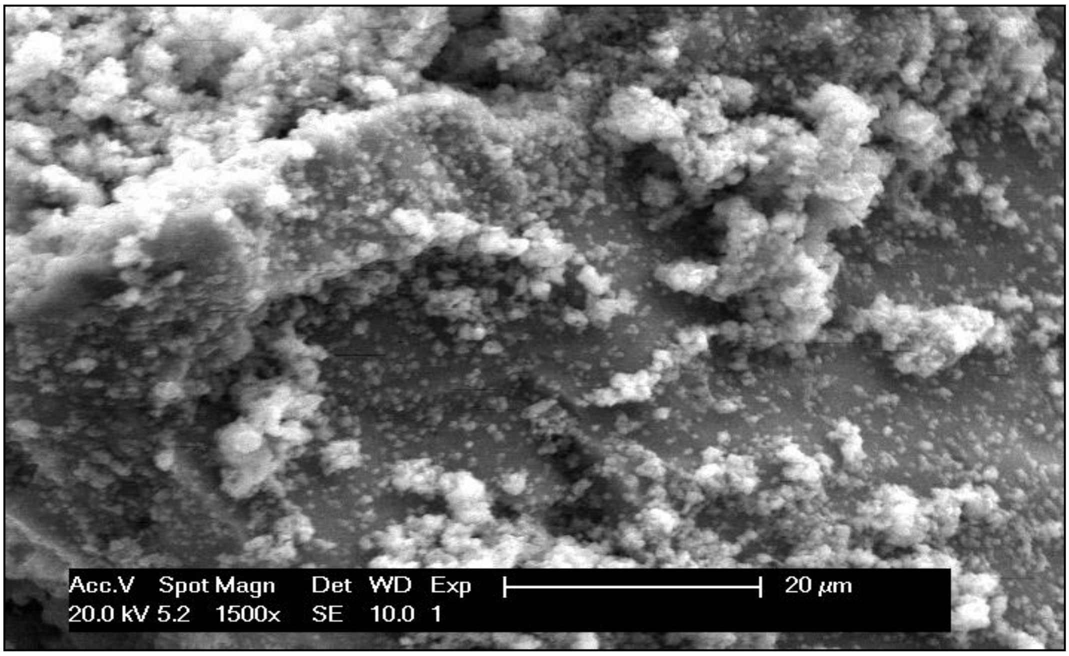


Figure 4.50: SEM image of mortar with 10% precipitated $CaCO_3$ at 56 days (27-90)

4.10.7 Calcitic Filler Modification Effects on Microscopy Development in 33°C - 90% RH

Figure 4.51, 4.52, 4.53, 4.54, 4.55, 4.56, 4.57 and 4.58 illustrate the modified lime mortar pore development cured in 33°C - 90% RH condition. Hexagon prisms of calcite can be identified as early as day 7 but the development seemed featureless. The crystalline formation appears irregular in shape and size.

Figure 4.51 show an image of mortar with 10% oyster shells modification. At 7 days, the formations of hexagon prism crystals are dense. It is observed that the formations of mortars cured in elevated temperature are denser than the lower temperature. A small number of needle-like crystals are identified.

Limestone mortar (see Figure 4.52) showed granulated structures with visible pores (black pixel or darker regions). Overall, the crystalline formation appears irregular in rhombohedral shapes and sizes. Individual calcite crystal surfaces appeared to be uneven; with smooth inter grown blocks with pits.

The marble mortar (see Figure 4.53) showed multi-layered prism structures with visible pores (black pixel or darker region). Overall, the crystalline formation appears irregular in rhombohedral shapes and sizes. Individual calcite crystal surfaces appeared to be uneven; with smooth inter dispersed cubic forms.

Figure 4.54 show the modified lime mortar with precipitated $CaCO_3$ pore development cured in 33°C - 90% RH condition at 7 days. Featureless formations with poorly defined hexagonal calcite crystalline forms are noted. It is observed that crystals have formed in a jagged manner. It is observed that a small numbers of acicular crystals of aragonite are identified (in circle).

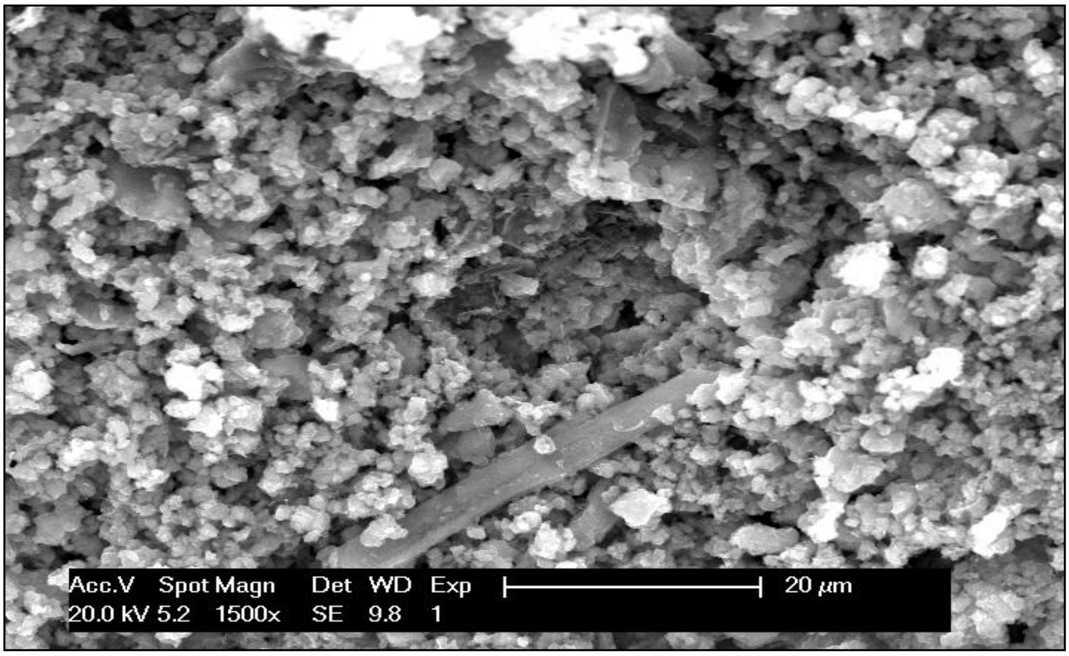


Figure 4.51: SEM image of mortar with 10% oyster shells at 7 days (33-90)

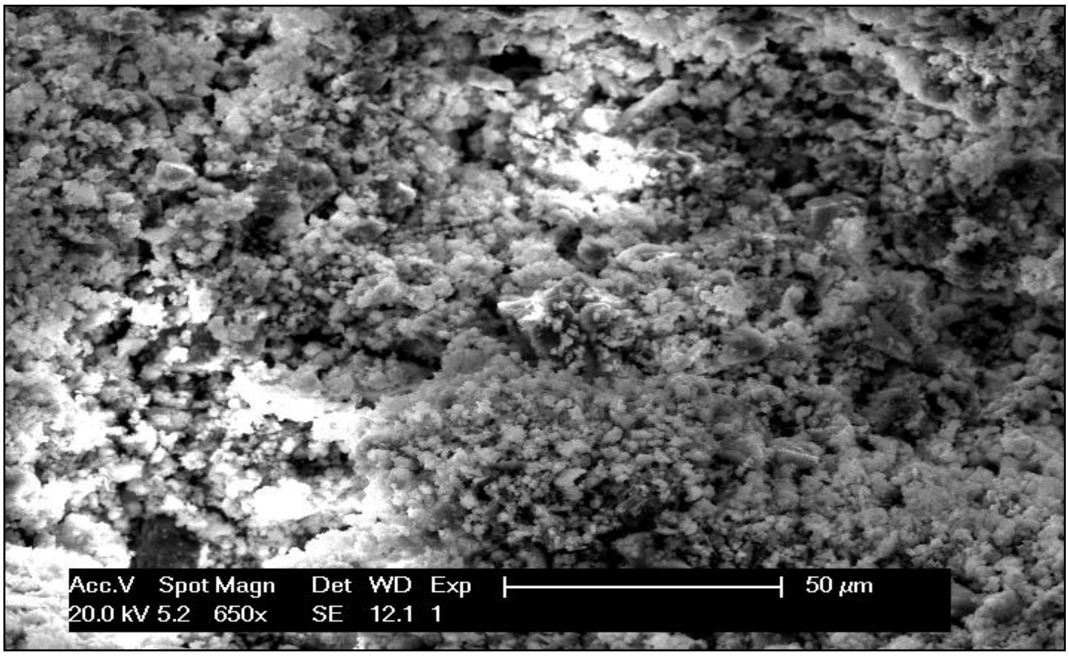


Figure 4.52: SEM image of mortar with 10% limestone at 7 days (33-90)

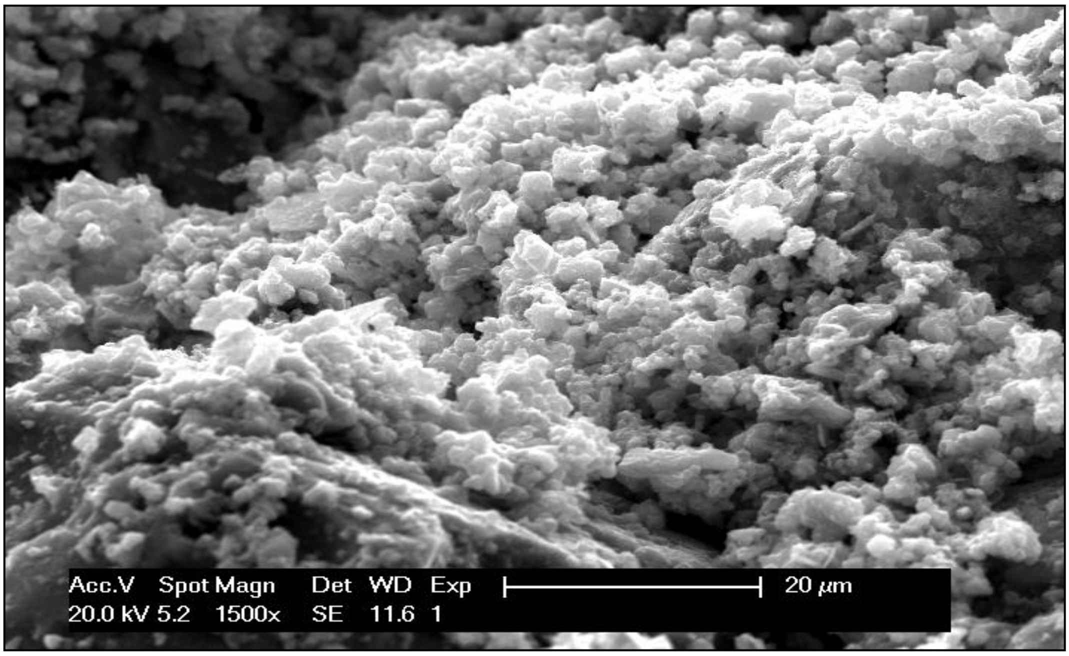


Figure 4.53: SEM image of mortar with 10% marble at 7 days (33-90)

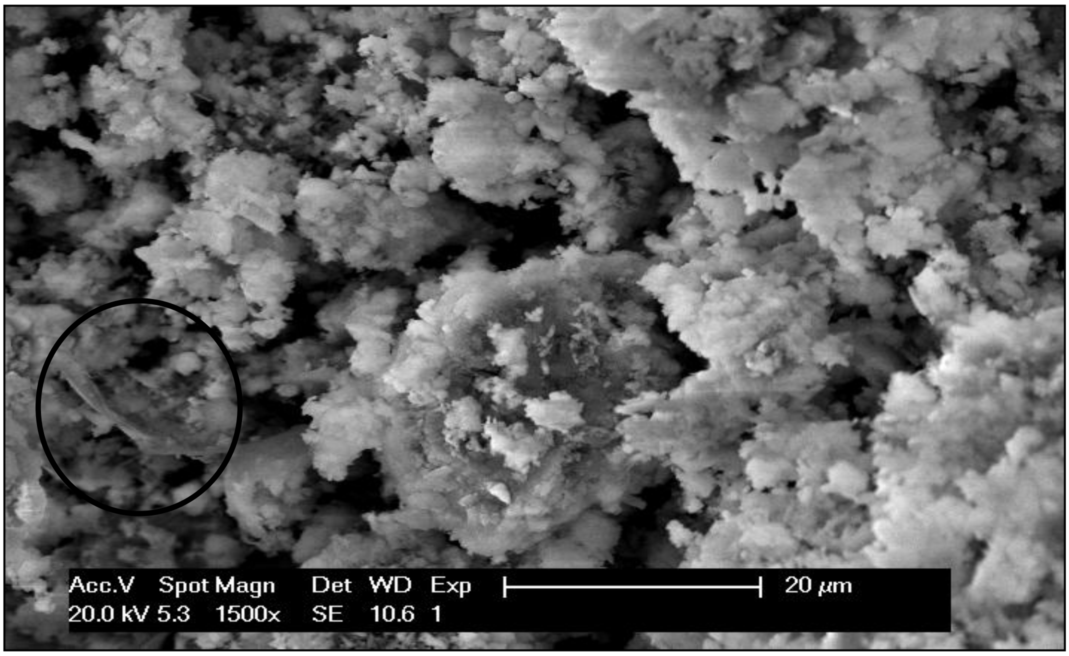


Figure 4.54: SEM image of mortar with 10% precipitated $CaCO_3$ at 7 days (33-90)

Towards the end of testing period (56 days), visible hexagon calcite prisms and products of hydration can be seen in all mortars (Figure 4.55, 4.56, 4.57 and 4.58).

Figure 4.55 show an image of mortar with 10% oyster shell modification. The formation of mixed crystal forms; granulated (on the left) and multi-layered calcite plates (on the right) are present.

Limestone mortar (see Figure 4.56) showed multi-layered granulated structures with no visible pores. Columnar crystals were identified (in circle). Overall, the crystalline formation appears irregular with rhombohedral shapes and sizes.

Marble mortar (see Figure 4.57) showed interspersed prism structure on the surface of aggregates. Overall, the crystalline formation appears irregular with rhombohedral shapes and sizes. Individual calcite crystal surfaces appear to be uneven; with smooth interspersed cubic forms.

Figure 4.58 show the modified lime mortar with precipitated $CaCO_3$ pore development cured in 33°C - 90% RH condition at day 56. The image shows the formation of varied crystal structures. Needle-like crystals are evident although the numbers are minimal. The production of a featureless formation and hexagonal calcite crystalline forms are distributed throughout. These specimens formed the largest calcite prisms and most dense surfaces compared to other specimens in 33°C - 90% RH condition.

The porosity gradually decreases with increasing distance from the interface. Even the modified mortars matrix appeared to be much denser, and the interfacial transition zone cannot be readily distinguished. It is observed that the specimens cured in this climate produced the densest calcite growth of all three climates.

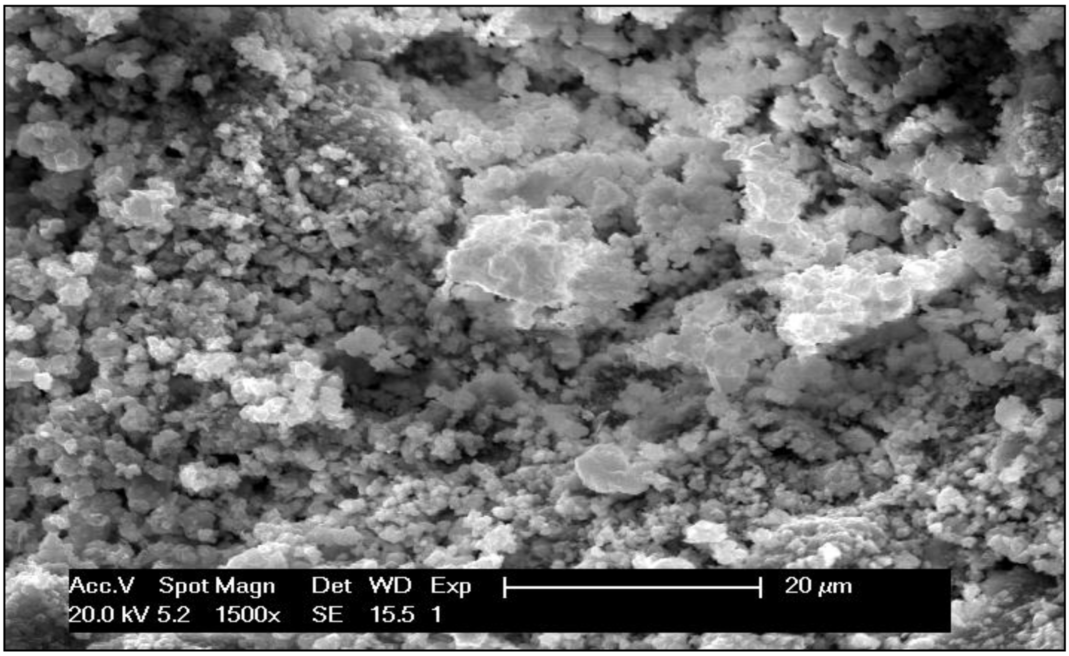


Figure 4.55: SEM image of mortar with 10% oyster shells at 56 days (33-90)

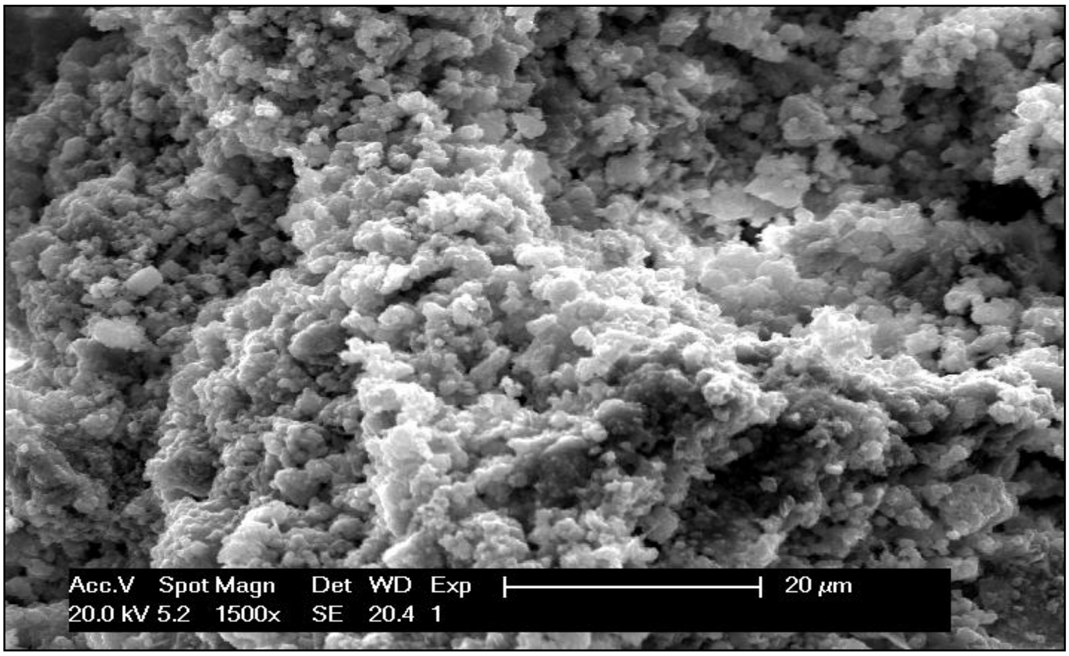


Figure 4.56: SEM image of mortar with 10% limestone at 56 days (33-90)

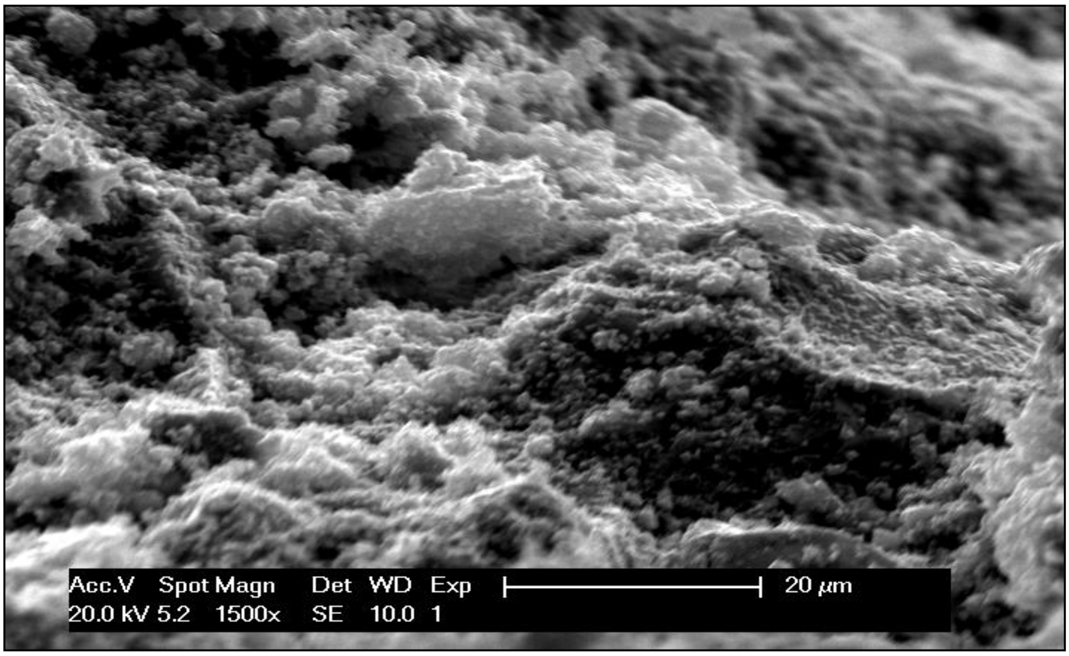


Figure 4.57: SEM image of mortar with 10% marble at 56 days (33-90)

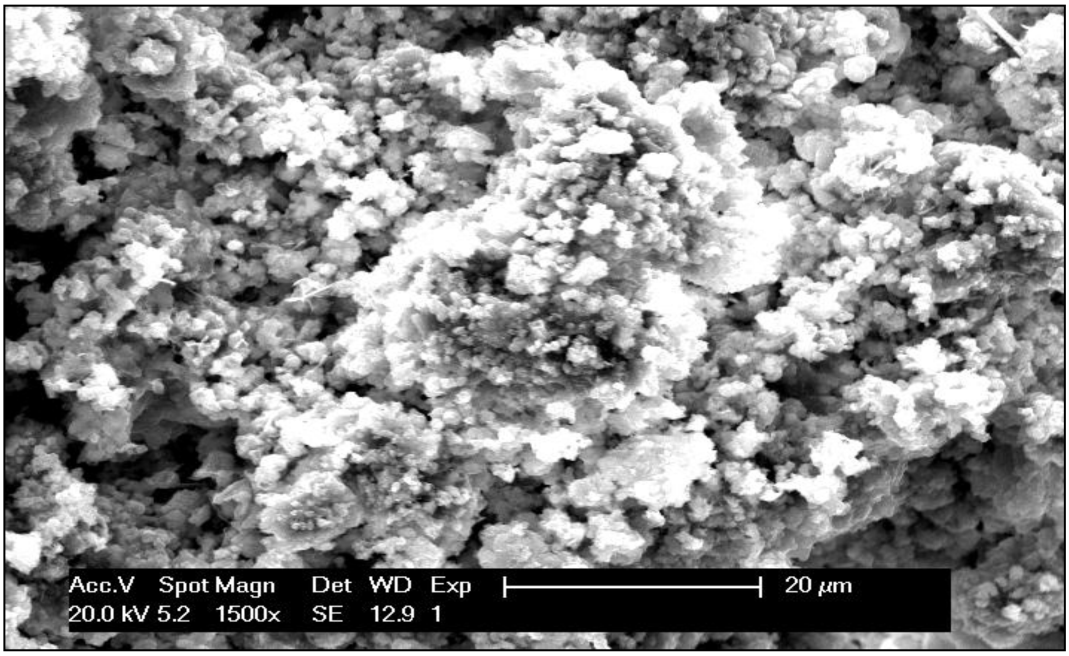


Figure 4.58: SEM image of mortar with 10% precipitated $CaCO_3$ at 56 days (33-90)

4.10.8 Summary

The SEM study set out to determine the pore structure development of modified mortars. One pronounced finding was the identification of large size calcite platelets in precipitated calcium carbonate mortars compared to other specimens. This technique illustrates the pore structure difference between specimens' ages but differences between the calcitic fillers in the mortars are difficult to detect.

4.11 Summary of Finding - Physical Properties

The effects of seeding materials undoubtedly vary with type. This is possibly due to variations in trace element chemistry and in physical form/crystallinity. In general, calcitic materials have a positive influence on the strength development and rapidity of carbonation of the natural hydraulic lime mortars exposed to high humidity and temperature environments. The following can be concluded from the physical characteristic investigations;

a. Experimental results indicate clear differences between the seeded specimens and the control samples with regards to the development of both flexural and compressive strength;

b. The relationships between the water absorption rates and time are valid but the gradient (sorptivity) varied with the type of calcite fillers and time. In addition, it has been shown that seeding reduces sorptivity;

c. At 28 days, sorptivity coefficient (*k*), of all mortars is in range of;

    i. 2.0 – 2.5 at 20°C – 60% RH;
    ii. 1.6 – 3.0 at 27°C – 90% RH;
    iii. 2.0 – 3.7 at 33°C – 90% RH;

d. Morphological observations revealed that the crystalline formation appears irregular in shape and size. The surfaces of the calcite crystals appear uneven, while the needle-like crystals have developed in a jagged manner;

e. High temperature also played a significant role in accelerating the hydration process and calcite growth. Elevated temperatures produced featureless calcite formations that might cause a strength loss.

CHAPTER 5
DISCUSSION

5.1 Introduction

The discussion of both the control and calcitic filler modified Natural Hydraulic Lime (NHL) mortars are presented within this chapter. The discussion is based on the results of 135 mortar specimens cured initially in a controlled environment (temperature and humidity) of 20°C - 60% RH (20-60). These parameters were then elevated to 27°C - 90% RH (27-90) and 33°C - 90% RH (33-90). In this chapter, the discussions are divided into 12 sub-topics. The sub-topics are presented in the following manner;

a. The effects of high temperature and humidity on natural hydraulic lime mortar (Section 5.2)
b. The chemical properties of modified natural hydraulic lime mortars
    - Moisture loss (Section 5.3)
    - pH value (Section 5.4)
    - Carbonation depth (Section 5.5)
    - Summary - Chemical Properties (Section 5.6)
c. Part Two: The physical properties of modified natural hydraulic lime mortars
    - Flexural strength of each mortar type at each time interval (Section 5.7)
    - Compressive strength of each mortar type at each time interval (Section 5.8)
    - Sorptivity tests for each mortar type (Section 5.9)
    - Micro-structural changes through scanning electron microscopy (SEM) (Section 5.10)
    - Summary - Physical Properties (Section 5.11)
d. Other factors influencing the modified mortars performance (section 5.12)
e. Reviews on findings (section 5.13)

5.2 The Effects of High Temperature and Humidity on Natural Hydraulic Lime Mortar

This study has investigated the effects of curing the control samples of lime mortar in three temperature and humidity conditions (20°C -60% RH; 27-90% RH; and 33-90% RH). There was a significant performance difference between samples cured in the standard conditions (20°C - 60% RH) and those in the elevated temperature and humidity (27 - 90% RH and 33 - 90% RH).

5.2.1 Carbonation Depth

The results of carbonation depth (see Figure 4.1) of this study indicate that temperature is one of the parameters affecting the rate of mortar carbonation. Carbonation leads to the production of calcium carbonate which facilitates the hardening of the mortar. The results in this experiment show that curing time influenced carbonation. Interestingly, mortars cured in 27°C – 90% RH showed superiority in carbonation when compared to 20°C – 60% RH and 33°C – 90% RH. Mortar cured at 27°C – 90% RH required only 14 days to reach full carbonation. The results suggest that this curing condition is conducive for the formation of calcium carbonate ($CaCO_3$). The creation of a favourable carbonic acid rich environment yields transformation of portlandite ($Ca(OH)_2$) into calcite.

At lower temperature (20°C – 60% RH), the time required for full carbonation was significantly longer (double at 28 days) compared to 27°C – 90% RH. Based on the results, mortars can achieve accelerated carbonation at 27°C – 90% RH.

The positive benefits of temperature upon carbonation reactions correlate with work by Moorehead (1986), Ashurst (2002), Allen et al. (2003), Lawrence (2006), Ball et al. (2009) and Ball et al. (2010). They reported that carbon dioxide diffusion is depending by the ambient conditions. It is because carbon dioxide molecules move faster in higher temperature. On the other hand, the diffusion rate of carbonation is slower in lower temperature condition.

Carbonation rates increase with temperature rise due to lime's inherent thermodynamic properties (high carbonation temperature, high CO_2 carrying capacity) (Materic and Smedley 2011). As the temperature increases (to 33°C), the water interaction with the solid surface increase and the process of carbonation rapidly initiates. After high, long term temperature exposure the materials dehydrate thus inhibiting carbonation of $Ca(OH)_2$.

The carbonation process in the 33°C – 90% RH environment was prolonged. This was associated with the negative influence of high humidity on carbonation. Importantly, the rate and extent of carbonation was largely independent of time but dependent on temperature. This conclusion concurs with Materic and Smedley's (2011) work on high temperature effects on $Ca(OH)_2$. Lime hydration was shown to reactivate when placed in the presence of humid air at ambient temperatures (Fennell et al. 2007).

5.2.2 Flexural Strength

As established in the literature review, flexural strength is a measure of a mortar to resist failure in bending. The results (see Figure 4.2) illustrate that curing temperature is one of the parameters affecting the rate and development of flexural strength in mortars.

It was shown that, due to the carbonation process (mortar hardening) the mechanical strength of the mortars increased with extended curing times. The carbonation reaction was more apparent in later curing time because of increased binder content and porosity which favours the diffusion of the carbon dioxide into the mortar where portlandite is still present to carbonate (Van Balen and Van Gemert 1994). This clearly concurs with the accepted body of knowledge in this area (Allen et al. 2003). This is true for the mortar strength at 14 to 28 days cured at 27°C – 90% RH. Mortars cured at 33°C – 90% RH had the lowest flexural strength development most likely associated with a delayed carbonation rate inhibited by very high and sustained moisture contents that hindered carbon dioxide diffusion (Steffens et al. 2002). However, Cizer et al. (2007) and Cizer et al. (2008) concluded that flexural strength of modified mortar is strongly depending on the types of seeded materials and mortar's porosity.

Conversely, the strengths determined at early ages (28 days) are not conclusive because the mortars were strongly influenced by the water content adopted for the mix. A clear relationship exists between water ratio and strength (Allen et al. 2003, Poon et al. 2004, Taylor 1997). Most of the mortars were still losing water at 28 days curing (see Figure 4.5, 4.6 and 4.7).

Lanas and Alvarez-Galindo (2006) established a hypothesis that would go some way to explain this situation in which they show that the mortars exhibit the highest strength value when a certain amount of calcium hydroxide remains un-carbonated. This is supported by observation at 14 days at 27°C – 90% RH, 28 days at 20°C – 60% RH and 42 days at 33°C – 90% RH. The decrease of a small amount of un-carbonated calcium hydroxide produces a slight reduction in mortar strength. However, without thermo gravimetric analysis, the specific amount of calcium hydroxide cannot be accurately determined.

5.2.3 Compressive Strength

The experiment was designed to determine the effect of temperature, curing time and materials modification on the compressive strength of the mortars. The results (see Figure 4.3) of this study indicate that temperature and curing time affecting the mortars compressive strength. At 7 days the mortars cured at 33°C – 90% RH exhibited the highest strength; followed by 27°C – 90% RH and 20°C – 60% RH. Contrary to expectations, the strength development at 14 and 28 days contradicted with the earlier findings. At the end of curing period, mortars cured at 27°C – 90% RH exhibited the highest strength, followed by 20°C – 60% RH and 33°C – 90% RH.

When evaluating the compressive strength development, it is logical that the aforementioned factors influencing the performance of flexural strength will also be pronounced here. The carbonation rate influences the strength development (Allen et al. 2003). As the calcium hydroxide converts into to calcium carbonate (calcite), the compressive strength increases with time. This is to be expected and conforms to an accepted understanding of the mechanisms of strength development in lime mortars during curing process as reported by Ward-Harvey (2009), Allen and Iano (2009) and Taylor (2002). Moropoulou et al. (1997) indicate that the occurrence of crystalline calcite in lime mortars results a porosity decrease and a strength increase .

Prolonged high temperature curing over longer time frames caused the mortars to lose strength. Mortar that has been exposed to elevated temperatures accelerated hydration resulting in non-uniform distribution of products of hydration. This resulted in increased of porosity and an increase in early stage of compressive strength. However, a decrease in longer strength development was noted. These findings correlated with Ezziane et al. (2007) who observed the strength loss evolution in elevated temperature and proposed mineral admixtures in the mortar as solution. The presence of some mineral admixtures in the mortar modifies the hydration kinetics, reducing the heat evolution and producing additional C-S-H.

5.2.4 Sorptivity Test

A strong relationship between lime mortar and sorptivity has been reported in the literature (Hall et al. 1995, Hall and Hoff 2002, Hall and Hoff 2012, Dane and Topp 2002, Appels 2013). Previous studies have emphasised the importance of a mortar to absorb and transmit water through capillary suction. The results (see Figure 4.4) of this study show that curing environment and time are not affected by the water absorption rate and sorptivity coefficient.

After 7 days of curing, mortars subject to 27°C – 90% RH showed the highest sorptivity. Although the samples subject to the high humidity of 27°C – 90% RH and 33°C – 90% RH are the same, it was noted that the temperature effects leads to altered pore structure and therefore greater sorptivity. This was most likely due to the favourable environment created for the development of the products of hydration (Barnes and Scheetz 1991).

Temperature difference between specimens 33°C – 90% RH and ambient room temperature (once it exposed outside the curing cabinet) may have further modified the sorptivity. In order to attain equilibrium with the ambient air temperature the specimens (33°C – 90% RH) would release a certain amount of moisture to the environment. As a result, moisture liberation and loss attempting to attain equilibrium would result in lower moisture content in the samples. This would influence their absorption during the sorptivity experiments.

The mortar samples cured at 20°C – 60% RH exhibited the lowest sorptivity compared to the other elevated curing environments. Lower humidity is not always associated with an increase in sorptivity due to the complexity of matrix development in the structure as a function of composition and hygrothermal conditions promoting or arresting growth. Based on scanning electron microscopy (SEM) analysis of the specimen cured at 20°C – 60% RH irregular shapes and sizes of crystal structures were noted.

Specimens cured at 33°C – 90% RH were associated with a smaller but more homogeneous and regular shaped crystal structure as opposed to specimens 20°C – 60% RH. It would be logical to assume that these experiments yielded size inconsistencies of the crystal structures leading to lower water absorption. Hence, the variation in the physical characteristics associated with curing led to sorpivity differences.

As the curing time increased, the mortar sorptivity coefficient, *k* in 27°C – 90% RH gradually decreased. The decreases were not significant (2.95 to 2.62). Conversely, sorptivity in 20°C – 60% RH and 33°C – 90% RH gradually increased. These mortars reached their maximum sorptivity at day 28 before gradually decreasing. The relationship with curing environment and sorptivity was noted up to 56 days.

In conclusion, the general effect of high temperature exposure upon sorptivity results was to produce higher values and greater overall water absorption. This conclusion is supported by Kerr (2008) who suggested other plausible factors such as water:binder ratio and binder content to be considered which may affect the damage to the pore structure from the different development of products of hydration.

5.2.5 Summary

The mortars were observed to set and harden as a result of combined binder hydration and carbonation. Strength development in the mortars was associated with the carbonation process that transformed portlandite into calcite. This is well understood and is generally associated with approximately 1 N/mm^2 increase in strength in the material (Allen et al, 2003). Additionally lime binder hydration contributes to the early stage strength development whist carbonation more favourable in later age due to porosity. For that reason, it is evident that the mechanical strengths increase with curing time.

Comparing these four tests revealed that mortars cured in a high temperature environment attain rapid initial strength, with subsequent decrease over time. This has the potential to jeopardize the quality of mortar produced. These finding also go some way to illustrate the difficulties of current use of NHL materials in high temperature and humidity environments such as tropical (hot and humid) regions.

5.3 Moisture Loss

Moisture loss in mortar is associated with hydraulic reactions and the compounding of water forming the composition of the newly formed hydrates. The relationship between temperature and hydraulic reaction rate is well established (Barnes and Scheetz 1991). In reactivity terms, increases in temperature and the introduction of high carbon dioxide concentrations has an altering affect upon the basic equilibrium kinetics. The Le Chatelier's principle explains this with moisture moving from a higher concentration towards areas of lower concentration (Fox and Whitesell 2003). This concurs with work by Bouasker et al. (2008) who associated chemical shrinkage at very early age with Le Chatelier's contraction. The temperature essentially creates a driving force for the reaction. The same can also be said for moisture transfer or diffusion. The hot environment both in terms of laboratory curing and practical applications will create a driving force to the external environment, drawing moisture with it.

The results obtained correlate with the Clausius–Clapeyron (Equation 5.1) relationship that explains the phase transition between two phases of matter of a single constituent (Ishida 2009). It has been shown that the heat of sorption and Clausius–Clapeyron formula explains that the lower the temperature, the higher the amount of water will be absorbed by the mortar (Poyet and Charles 2009).

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\Delta v}$$

(Equation 5.1)

Where;

$\frac{dP}{\mathrm{d}T}$ is the slope of the tangent to the coexistence curve at any point, L is the specific latent heat, T is the temperature, and Δv is the specific volume change of the phase transition.

5.3.1 Assessment on Temperature

Although the modified mortars have improved properties, it appears that they have an increased moisture loss rate, especially in higher temperature. In 33°C - 90% RH, a steep slope in the data showed a rapid moisture loss as compared to other climates that have lower temperatures.

Rapid moisture loss is known to be associated with crack development during hardening. This is associated with the specimens experiencing a drying shrinkage effect. It was discovered that specimens cured in 27°C - 90% RH condition experienced the greatest early stage shrinkage. It is believed that due to prolonged high temperature exposure, the specimens in both experimental climates experienced shrinkage especially at the edges of the materials. An insufficient quantity of water required for full hydration and carbonation reactions could cause a consistent reduction of volume and loss of favourable physical characteristics.

A high temperature leads to rapid drying. This water loss was less pronounced in 27°C - 90% RH. This is due to the high humidity (almost saturated) compensating the moisture loss from the mortar. However, after prolonged exposure to high temperature, the moisture compensation cannot overcome the tensile stresses generated by volume changes. At 7 days, the tensile strength was still developing. Cracks develop when the tensile stress exceeds the material resisting capability. Therefore, the mortars suffered a drying shrinkage effect.

Prolonged exposure to elevated temperatures increases the amount of moisture loss. It was observed that modified mortars lost significantly more water than un-modified mortars in every age. This indicates that the sensitivity of hydration reactions to temperature in modified mortars with calcite fillers is more significant than un-modified materials.

5.3.2 Calcites Solubility

Moisture loss from the mortar may be possibly associated with the solubility of calcium carbonate that is poorly soluble in pure water (999.9720 kg/m^3 at 4°C) (Othman 2005). Due to the low rate of solubility of calcite, the amount of unbound water increases and is therefore prone to loss via evaporation. Even though the percentage of moisture loss of all the specimens is under 18%, a significant variation can be observed between the modified and un-modified mortars.

It has been suggested by Hauser (2002) that carbon dioxide increases calcite solubility. This is verified by the rapid rate of carbonation of modified mortars at 28 days. It was evident that when carbon dioxide was injected (450-500 ppm) into the curing chamber that a slight soluble effect on calcite was noted. These experimental results conform to accepted solubility kinetics that an increase of solubility of calcium carbonate is associated with a decrease of temperature (Boynton 1980). Additionally, an increase of pressure and an increase of carbon dioxide partial pressure are also understood to affect performance and therefore the experimental results. This concurs with the principle of ‘open system reactions’ proposed by Lottermoser (2010) as stated in (Equation 5.2);

$$CaCO_{3\,(s)} + CO_{2\,(g)} + H_2O_{\,(l)} <=> Ca_2^{+}{}_{(aq)} + 2HCO_3^{-}{}_{(aq)}$$

(Equation 5.2)

5.3.3 *Chemical Changes*

Benachour et al. (2008) and Benachour et al. (2009) identified that drying shrinkage is caused by chemical changes. The different composition and particle sizes of materials in the modified mortar mixtures yielded high values associated with moisture loss compared to un-modified mortars. The moisture loss increased significantly due to the adjustment of the types and proportion of calcitic additives introduced into the different mortar formulations. It is well understood that the size of the aggregate has an indirect influence on the water content of mortar (Neville 2002). Additionally to the influence of wettability and water retentivity, high density aggregates and high modulus of elasticity of aggregates will increase the compressive strength and decrease the shrinkage of mortar. This finding is supported by Noguchi and Nemati (1995) who proposed an empirical equation on the relationship between compressive strengths and modulus of elasticity based on statistical analysis.

In this study, precipitated calcium carbonate specimens (6% and 10% substitutions) were shown to have the most significant water loss in both elevated climates. This may be due to the precipitated calcium carbonates relatively fine particle size. The increase in the surface area of the particle would have an influence upon water for hydration. Due to the fine size and relatively high surface area, the amounts of precipitated calcium carbonate would have a disproportionate influence on the properties of the mortars compared to their counterparts. This situation was reflected in precipitated calcium carbonate mortars requiring extra water for hydration.

5.3.4 *Conclusion on Moisture Loss*

Calcitic fillers have been shown to have poor water retaining properties. This is most pronounced in high temperature low humidity environments with high potential evaporation rates (Hall and Hoff 2002, Hall and Hoff 2012). Water retentivity is clearly important in terms of rheological properties of the mortar but also for facilitating the hydration and latterly the rapidity of the carbonation reaction. High moisture loss from modified mortars will negatively influence the precipitation reactions chemical changes in the mortars. Fine calcitic fillers such as precipitated calcium carbonate required supplementary water. This was to enable satisfactory workability due to its relatively large surface area. Clearly, processes to reduce water loss are important and can be undertaken by supplementary spraying.

5.4 pH

The pH values for all the mortars have been described in Section 4.3 (Table 4.1). All fresh mortars had pH 14 due to their high calcium hydroxide concentration. As a mortar surface reacts with carbon dioxide in air, the pH value slowly lowers due to carbonation. Differences in the pH values were noted at 7 days between the types of mortar and their respective calcitic fillers. The dissolution of calcium hydroxide and the formation of calcite lowered the pH and alkalinity in the mortar. All mortars in all of the simulated climates achieved pH of 7 at day 14. Although the changes in the pH values are small, there is a clear trend that can be distinguished.

5.4.1 Chemical Reactions

From the pH values attained, it was confirmed that the neutralization process with its respective exothermic reaction had taken place conforming to Equation 5.3 and Equation 5.4 (Lottermoser 2010). The reaction of calcium hydroxide with carbon dioxide is relatively rapid, producing a mortar that hardens quickly. However, reversal of (Equation 5.3) and (Equation 5.4) are possible when there is a change in temperature, loss of water or loss of carbon dioxide. The pH will continue to reduce with re-precipitation of carbonate, which in turn releases hydrogen ions.

$$CaCO_{3\,(s)} + H^{+}_{\ (aq)} <=> Ca^{2+}_{\ (aq)} + HCO_3^{-}{}_{\ (aq)}$$

(Equation 5.3)

$$CaCO_{3\,(s)} + 2H^{+}_{\ (aq)} <=> Ca^{2+}_{\ (aq)} + H_2CO_3^{-}\ (_{aq)}$$

(Equation 5.4)

5.4.2 Solubility Factors

As the solubility of calcium increases the mortar's pH will be lowered. The surface of the mortar had minimal moisture vapour movement, thus making the pH reading and carbonation depth more varied when compared with the other side of the specimens. Conversely, in a high humidity environment (90% RH), the excessive moisture will transport additional hydroxides (alkalis) to the surface and will cause the pH level to increase. This may potentially make the mortar weak due to a lack of calcium ions (Ca^{2+}) required for the formation of hydrates.

5.4.3 Hydration Process

The pH variations could be attributed to differences in materials characteristics and their properties with a corresponding influence on the extent of carbonation of the mortars. The general reduction of pH over time can be attributed to carbonation. For the first 7 days of curing, all the specimens' experienced atmospheric carbonation on their surfaces. The idealised CO_2 concentration enables rapid mortar carbonation, thus dropping the pH levels.

High temperature accelerates the rate of hydration and influences the pH value (Rasanen and Penttala 2004). It is possible that the prolonged exposure of the materials to the high temperature curing regime caused greater changes on the pH values. Continuous readings were taken until the end of the study to check any increase of pH value.

5.5 Carbonation Depth

The carbonation was observed in all the mortars and climatic conditions. The results showed that the temperature, relative humidity, curing time, nature and proportions of the seeding materials influenced the carbonation rate. The specimens cured in 27°C – 90% RH reached the full carbonation depth 14 days earlier than the specimens in control climate (20°C – 60% RH). The higher temperature (33°C– 90% RH) environment that the specimens were subjected to showed the slowest carbonation profile off all climates. Whilst slow the carbonation followed a linear function.

The carbonation of calcium hydroxide at high temperatures appears to be more complex. From the data obtained, carbonation conversion was found to be higher when calcium hydroxide was carbonated at elevated temperatures when compared to conventional curing temperature of 20°C – 60% RH. The 33°C – 90% RH produced the lowest carbonation depth over time. This may be associated with the carbonation process being delayed in high temperature environments. The retardation of carbon dioxide gas solubility in the liquid phase may be hindering rapid conversion. As solubility decreases, with an increase in temperature the carbon dioxide cannot remain in the mortar because there is simply no mechanism to hold it in suspension.

5.5.1 Induced Environment

High concentration of carbon dioxide plays the biggest role in the carbonation process (Lawrence 2006, Lyons 2010, Bertos et al. 2004, Lange et al. 1996). This clearly facilitates the conversion of $Ca(OH)_2$ into calcite (Moorehead 1986).

Carbonation of calcium hydroxide is greatly influenced by the presence of water adsorbed (from the spraying regime) from the surface of calcium hydroxide. The presence of adsorbed water by mortar is a controlling feature of the kinetics and a major influence on the carbonation of calcium hydroxide (Beruto and Botter 2000). Carbonation depends on the presence of water and occurs very rapidly from the outer surface. This is especially pronounced in a saturated carbon dioxide atmosphere.

Modified mortars with calcitic fillers were found to have higher carbonation rates compared to un-modified mortars (see Figure 4.8, 4.10 and 4.13). This was most likely associated with the potential influence of fine calcitic fillers acting as a nucleation sites for precipitation. An additional consequence of this induced carbonation process was that it potentially accelerates as a result of the decrease in the calcium ion concentration associated with unsaturated (supersaturated) environments. Precipitation may lower the Ca^{2+} concentration and therefore stimulate the development of C-S-H associated with belite (Hewlett 2004). This phenomenon has been hypothesised and relates to the solubility kinetics and impermeable hydrate theory established by Odler (2006). These concepts concur with work by Cizer et al. (2007), Bakharev (1999), Benachour (2008), Ezziane (2007) and El-Turki (2007).

Conversely, the modified mortars did not have significantly different carbonation rates. This concurs with work by Cultrone et al. (2005) who suggested that the carbonation process was not significantly affected by additives but by the carbon dioxide concentration.

It can be concluded that temperature, water content and carbon dioxide concentration are the main contributing factors in determining the rate of carbonation. The data showed comparative trends for carbonation in both the control (un-modified) and modified mortars across the climates. The results obtained suggested a rather complex pattern.

5.5.2 Comparisons with Previous Works

It was suggested by Skoulikidis et al. (1995) and Skoulikidis et al. (1996) that 6% of seeding is sufficient to increase the carbonation rate. This concurs with the findings of this research. The seeding of 10% calcitic materials did not result in any significant benefit to the mortars carbonation rate. The increase of carbonation rate was associated with a decrease in the particle size of the seeding materials. This concurs with the Hall-Petch equation.

5.6 Summary - Chemical Properties

From the data obtained, moisture loss in the mortars is most likely associated with the heat elevation. Moisture loss is also associated with solubility due to calcium carbonate's relative poor solubility making the amount of unbounded water relatively high and therefore making the material more prone to evaporation. Acceleration of hydration processes also contributed to rapid pH value reduction to pH 7 in initial 14 days. This is due to increased Ca^{2+}. Seeding material may minimize the effect of the dormancy period leading to deterioration of the Ca^{2+} ion layer as they are readily utilized in the formation of calcite through precipitation (Forster et al. 2013). All specimens had various values of pH due to differences in material's characteristics and properties and differences in the extent of carbonation of the mortars.

The carbonation process was associated with the carbon dioxide concentration, temperature and water content. 27°C – 90% RH showed an increase of carbonation rate, whilst 33°C - 90% RH results show conflicting results inhibiting the carbonation rate. The delay of carbonation is due to the decreasing carbon dioxide solubility. It is uncertain about the temperature threshold. The carbon dioxide concentration is the most important factor in carbonation. The increased CO_2 concentration should have resulted in greater rapidity over and above the natural rate of carbonation.

Clearly, the relationship between carbonation and calcitic fillers appears to be complex and inconclusive for the majority of materials. Carbonation under natural environmental conditions would result in slower carbonation reactions compared to the artificial environment. Further investigation is required before undertaking product modification.

5.7 Flexural Strength

This experiment was established with the aim of assessing the influence of calcitic filler as seeding materials in mortars cured in high temperature and humidity environments. The results of these experiments (see Figure 4.13, 4.14 and 4.15) showed that seeding did influence the flexural strength performance of mortar. Four types of calcitic fillers were used in this study; oyster shells powder, limestone powder, marble powder and precipitated calcium carbonate powder. Each type was subdivided into two amounts of seeding material, namely; 6% and 10%. From the data obtained, 88% of the total specimens in all climates with 10% of seeding recorded a higher flexural strength value than their 6% seeding amount counterpart.

5.7.1 Climatic Factors

At 27°C – 90% RH, all the mortars gained strength for the first 14 days. Seven out of 9 formulations gained the maximum strength at 14 days whist the other two reached maximum strength at day 28. Initially, the modified mortars had no significant strength difference compared to the non-modified mortars. However, as the curing time progressed the modified mortars’ strength did increase significantly, surpassing the control (un-modified) mortars.

Considering all the modified mortars, 33°C – 90% RH, gave the lowest strength. In general, all mortars gained strength for the initial 14 days in which five out of nine formulations reached the maximum flexural strength at day 42. Precipitated calcium carbonate yielded the highest flexural strength until the end of curing period. Only mortars with marble (both 6% and 10%) have no significant strength development after 28 days of curing.

Based on the data obtained, mortars exposed to higher temperature and humidity environments gained rapid strength but consequently experienced strength loss after 28 days. Modified mortars with calcitic filler is would enable mitigation against adverse effects of flexural strength loss in these materials. However, the comparisons between the fillers can be complex as each formulation yielded a different strength and trend.

5.7.2 Influence of Porosity

In this study, the precursor calcite materials for seeding in mortar manufacture were in a powdered form and would be expected to reduce the overall porosity. Furthermore, during the setting process (introduction of heat treatment), much of the porosity will be eliminated due to hydration and carbonation and associated densification. The porosity of the materials will vary significantly from early stage through to full hydrated, hardened materials. Clearly, the pore structure will play a significant role on the flexural response and other physical characteristics.

Porosity is damaging to the mortar's flexural strength for two main reasons; (i) pores reduce the cross-sectional area across which a load is applied and (ii) porosity acts to concentrate stress. The influence of porosity on strength is therefore relatively significant. The correlation between flexural strength and porosity was observed by Callister (2010) who suggested that 10% porosity volume will decrease the flexural strength by 50% for the measured value for the non porous materials.

5.7.3 Non-symmetry Cracks

40% of the total specimens had non-symmetry cracks (see Figure 4.14). In theory, a mortar would achieve similar flexural strength range due to (i) its homogeneity in the materials used and (ii) consistent proportions and mix regime. Based on the cracks, it is reasonable to assert that some of the specimens were not homogeneously casted into mould, yielding flexural strengths that were variable across the sample. Another factor that could change the mortars' flexural strength is defective structure, or that there was a consistent asymmetry in the loading.

5.8 Compressive Strength

These experiments were designed to determine the effect of calcitic filler as seeding materials in mortar cured in high temperature and humidity. The results of these experiments (see Figure 4.20, 4.21 and 4.22) showed that temperature, humidity, curing time and seeding materials influenced the compressive strength performance of mortar. Between 7 - 14 days at 27°C – 90% RH, it was observed that all modified mortars exhibited rapid early strength gain. This is reflected in a steep positive gradient of the graph. Half of the modified mortars achieved maximum compressive strength at day 42 as compared to un-modified mortar. The formulations that yielded the strongest mortars were precipitated calcium carbonate 6% and 10%. At 33°C – 90% RH, all the mortars experienced a slow early development up to 28 days. However, most of the mortars exhibited rapid changes in strength gain or strength loss after 28 days, until the end of the testing period.

5.8.1 Rewetting

It was observed that some of the modified mortar specimens lost their strength in the middle of the curing period (28 - 42 days), beyond which they regained their strength. When all the moisture has been absorbed and dried out, further bonds are formed in the mortar paste. This bonding allowed the mortar to continue gaining strength. Conversely, dehydration reduced the progress in the formation of the products of hydration and therefore was associated with strength loss. On rewetting, there is a rapid strength loss caused by the absorption of water, followed by a recovery, in the long term, strength that was commensurate to expected performance.

5.8.2 Effectiveness Factors

It can be observed that the performance of each modified mortar depends on the calcite types. The effectiveness of calcitic filler can be evaluated based on two factors; (i) calcitic composition (calcium carbonate content / purity) and (ii) particle size.

5.8.3 Purity

All calcitic fillers used have similar chemical compositions (in percentage terms). The purity of the seeding material is expressed by calcium carbonate ($CaCO_3$) equivalence. Pure calcium carbonate has an equivalence of 100%. It is known that precipitated calcium carbonate (PCC) contains 100% calcium carbonate with 99.99% purity. Conversely, calcium carbonate content of oyster shells, limestone and marble varies in between 90% - 97% with the minerals considered as trace element. The differences are based on occurrence and the location of the materials.

It was hypothesized that the incorporation of calcitic aggregate influences the compressive strength in hydraulic lime mortars in high temperature and humidity environments. Precipitated calcium carbonate yielded significantly higher strength than the un-modified mortars, thus reducing the adverse effects of mortar strength loss. Use of oyster shells, limestone and marble with similar purities were expected to attain comparable results as precipitated calcium carbonate. These materials showed higher strength development than the control (unmodified) mortars, but the overall performance was complex and inconclusive. The least effective calcitic filler was marble. It is believed that the ineffectiveness was due to its relatively low calcium carbonate purity. Based on XRD analysis, the material has high quantity of dolomite. This would have an influence on the carbonation process. Marble and limestone are chemically identical ($CaCO_3$) but differ in physical properties. Limestone is sedimentary rock with smaller particles of calcium carbonate and is thus more porous and more workable thus making it more effective than marble as calcitic filler.

5.8.4 Particle Size

The second factor is particle size that was believed to strongly influence the performance.

Natural calcites (oyster shells, limestone and marble) that had been used were 60 mesh (0.250 mm) whilst precipitated calcium carbonate was 100 mesh (0.149 mm). According to Peters (1996), the effectiveness of calcium carbonate increased to 100% for seeding materials with <60 mesh. This would concur with these results in which mortars with precipitated calcium carbonate gained the highest strength as compared to other modified mortars in high temperature and humidity environment.

From the compressive strength tests results it was evident that the fineness of seeding materials plays an important role in the effectiveness of performance on modified mortars. The efficiency of calcitic filler will depend upon the particles size. This is in agreement with observation by Bui et al. (2005) and Cheung et al. (2011).

Calcium carbonates relatively small particle size and therefore dissolution rate altered its effectiveness. The relationship between surface area and increasing solubility is well established. This is due to the finer grades of seeding materials having a significantly greater surface area per unit weight of materials than the coarser grade. The hardness of marble made the preparation more difficult and therefore the attainment of a relative uniform fineness for addition affected the solubility and reaction time. Hence, the larger the particles size of marble to the greater the reduction in the efficacy of seeding (by approximately 60%).

5.8.5 Seeding Quantities

For modified mortars with natural calcitic fillers (oyster shells, limestone and marble), there were no significant differences in strength development in between 6% and 10% substitutions. However, modified mortars with 10% precipitated calcium carbonate produced a significantly higher strength than their 6% substitution counterparts. This is due to the quantity of precipitated calcium carbonate and its purity.

Due to the higher density and larger particle sizes of the natural calcites, the difference between 6% and 10% is not significant. This goes some way to explain why the strength performance of the mortars with between 6% and 10% of natural calcite was not significantly different. This concurs with work by Skoulikidis et al. (1995) and Skoulikidis et al. (1996) who indicates that 6% of calcium carbonate (in the form of paste, emulsion or solution) is sufficient to increase the rate of carbonation. In addition, the inclusion of more than 6% can lead to a decrease of mechanical properties.

5.8.6 Shear Stress

Compressive forces in mortars act in same manner as atomic bonding (Taylor 2002). Compression induces stresses and tensile strain leading to the manifestation of tensile stress. The Poisson's ratio effect, ν is used to describe this phenomenon. Poisson's ratio is equal to the horizontal movement (two directions perpendicular to the direction of compression) as a proportional of the vertical movement.

Depending on the seeding materials, specimen shape and loading arrangement, compression may cause shear or tensile failure or the combination of two. Figure 5.1 illustrates the Poisson's ratio effect in compression. The tensile stress is at right angles to the applied compressive strength. Poisson's ratio effect is the reason the specimen cube will expand when compressive load is applied. The mortar tries to resist a change in volume as determined by the bulk modulus. A change in shape, is a indication of the shear modulus.

As a compressive load is exerted the crack is closed and the plastic zone in front of the crack does not play a role in fracture behaviour of the material (in fact there is no crack-tip plastic zone under compressive loading) tolerating a high level of pressure without the occurrence of fracture. In the case of compressive loading, the strong bonds between atoms are responsible for high compressive strength of the brittle materials; and this is especially it is true for mortar.

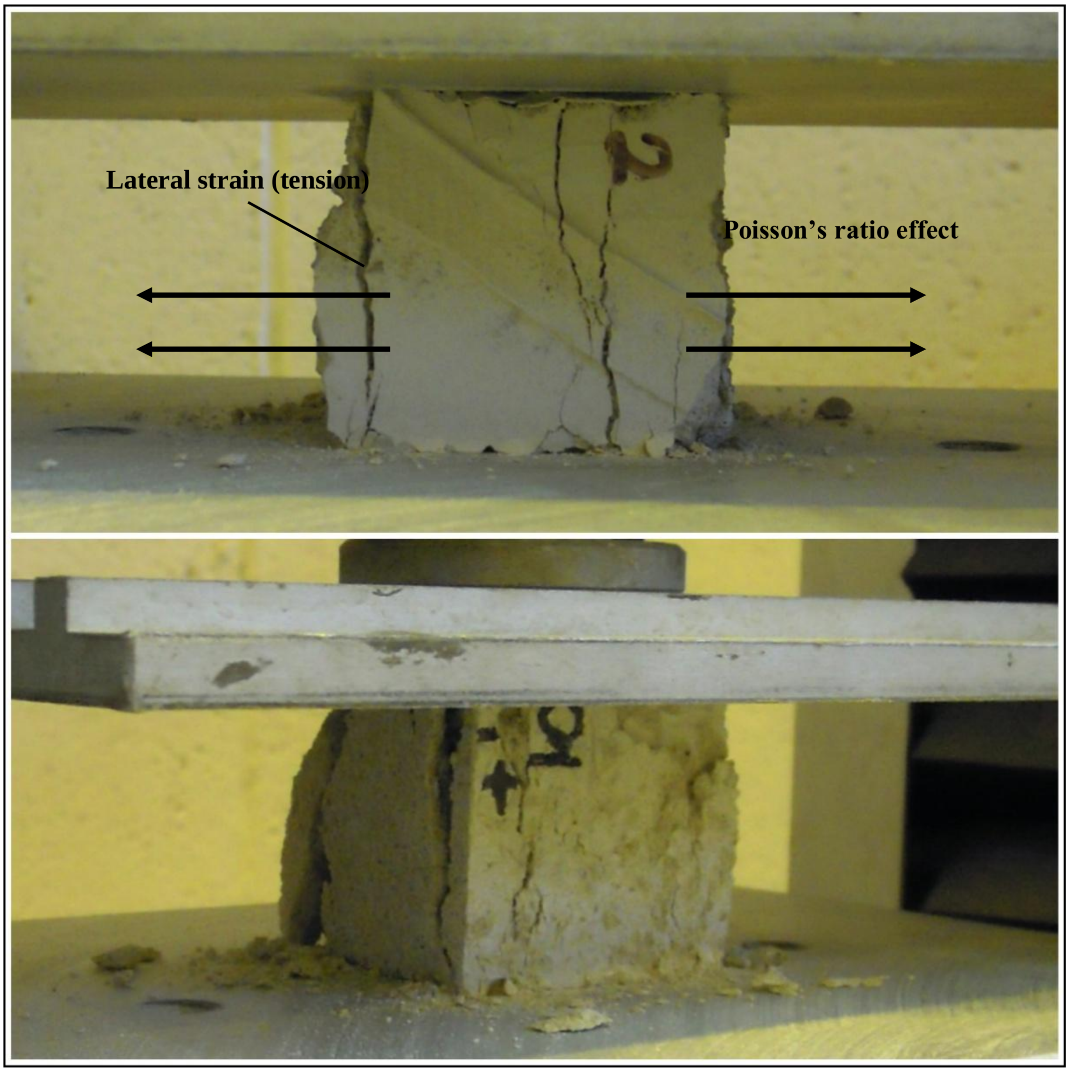


Figure 5.1: Poisson's ratio effect in compression stress; (above) front view; (below) side view

These tests were replicated by using metal pads in between the mortar specimen and the load plate (see Figure 5.2) to distinguish the effects of compressive strength testing variations. Insertion of metal pads above and below the specimens reverses the Poisson's ratio effect (inward movement) as the metal squeezed out sideway causing a tensile failure in the form of vertical crack at a very low stress.

Figure 5.2: Stress caused by platen restraint on a mortar cube during testing with metal pad

5.8.7 Bonding of Atoms

In solids, atoms become rigidly oriented in relation to one another. In many solids, there is some degree of crystallinity. Therefore the strength of bonding in a mortar underpins its mechanical / shear strength. It is understood that the relative importance of surface area of hydrate forms are ultimately responsible for the mechanical strength in the cementitious materials. Weak inter-laminar, inter molecular attraction known as 'Van Der Waals' forces that create a bond between the crystal structures that are cumulatively very significant (Damone 2010). The properties of all solid materials are derived from the properties of these bonds, although other effects often modify its strength.

The evaluation of micro-structure via scanning microscopy analysis (Section 5.10) enables qualitative determination. Additionally, the bonding between calcite and aggregates forms bonds between the materials. Modified mortars with calcitic filler produced denser crystalline formation. Based on the compressive strength strong bonds were formed. These interfaces are associated with adhesion between the surfaces. In addition, some of the mortars have twinned calcite crystals that are believed to increase the strength (Natalio et al. 2013). Due to the elevated temperature environment from the curing process, some of the crystals formed an amorphous form. This may create a weak inter-connectivity that may jeopardize the mortar strength.

5.8.8 Summary

Strength lost at 33°C – 90% RH was not significant compared to 27°C – 90% RH. At 33°C – 90% RH, only 25% of the modified mortars suffered strength loss at day 56. The performance of the mortars with calcitic fillers are complex (similar to flexural strength) but more pronounced at 33°C – 90% RH. The precipitated calcium carbonates (6% and 10%) are most effective filler. The marble (6% and 10%) are the least effective with average strength being not greater than 1N/mm^2 for the whole curing period.

From the data obtained, it can be concluded that temperature, humidity, curing time, calcitic filler proportions and size all influenced the mortar's compressive strength development. This indicates that higher early compressive strengths can be achieved at elevated temperature and humidity (Ezziane et al. 2007). However, the initial rapid strength development normalises over the longer term. Similar findings was also reported by Kim et al. (1998).

High temperature improves early compressive strength development. The hydrates formed do not however, have sufficient time to properly arrange and this may ultimately result in lower long term strengths. This phenomenon had been termed the 'crossover' effect (Carino 1994). Bakharev et al. (1999) reported that the more dense the precipitate deposits at elevated temperatures the greater the barrier for ion diffusion occurs. This adversely affects the microstructure and significantly reduces strength. Seeding materials may reduce the negative influence of the crossover effect due to its ability to induce Ca^{2+} precipitates.

5.9 Sorptivity

5.9.1 Water Absorption

Results are presented in Figure 4.23, 4.24 and 4.25, where the volume of the absorbed water per unit cross section (mm) is plotted against the square root of submerged time ($\text{min}^{0.5}$). The observations were made at the end of test period (56 days). The validity of the (Equation 3.3) was tested. Hypothetically, if the equation is valid, the graphs should generate a straight line and the capillarity coefficient and sorptivity would equal the gradient. This situation is valid for all specimens, in all climates with exception on mortars with precipitated calcium carbonate 6% cured in 33°C - 90% RH condition.

Variations in linearity were observed. This anomaly was identified by Hall et al. (1995) who explained that this phenomenon is most likely associated by newly formed hydration products that take place in the presence of water and cause an increase of effective grain size (via densification) and tend to block the micro pores. Consequently, water movement through mortar is hindered.

5.9.2 Sorptivity

The sorptivity behavior of seeding modified mortars was measured up to 56 days. The results in Chapter 4 (Figure 4.26, 4.27 and 4.28) illustrate that the un-modified mortars (control specimens) generally exhibited an increase of water absorption over other specimens in high temperature and humidity conditions. Overall, the sorptivity coefficient values of all mortars cured in all climates varied from 1 – 4 $\text{mm/min}^{0.5}$.

Further analysis showed that the most significant difference between un-modified and modified mortar can be seen in 33°C - 90% RH. It is believed that the temperature difference between specimens 33°C – 90% RH and ambient room temperature may have further affecting the sorptivity. In order to reach the temperature equilibrium the specimens released a certain amount of moisture to the environment. As a result, moisture loss from creates additional unfilled spaces in the pore for water to be absorbed during experiment. The sorptivity increased with the amount of evaporated water in the mortar.

Theoretically, a high moisture absorption value correlates to a weak mortar. This may be associated with the high numbers of micro cracks that lead to an interconnected porous structure. The results obtained from the control un-modified mortars had the highest sorptivity in the high temperature and humidity conditions. In addition, control (un-modified) mortars exhibited the weakest mortars of all the materials. It was observed that, the micro cracks and increased porosity in un-modified mortars, created weak points.

Results of modified mortars in high temperature and humidity show a low water absorption and sorptivity. The substitution of calcite materials as aggregates conferred better water absorption performance compared to control (un-modified) mortars. This is supported by De Oliveira et al. (2006) who undertook a comparative analysis of the sorptivity, indicating the formation of denser pore structures slowed down water movement during experiments. Sorptivity is therefore influenced by the connectivity of the pore network. It can be conclude that mortar modifications with calcitic filler can reduce sorptivity for mortars cured in high temperature and humidity.

Based on SEM images (shown in Section 4.10), it was observed that modified mortars had a denser crystal formation. That said, each calcitic material and formulation, cured in different climate conditions yielded distinctive results in the pore structure development. This is supported by Hanzic and Ilic (2003) that identified that materials with similar sorptivity, do not necessarily relate to similar capillarity functions and vice versa.

5.9.3 Physical Characteristics and Sorptivity

Attempts were made to correlate the sorptivity (as primary axis) to carbonation depth, and flexural strength and compressive strength (as secondary axis) of limestone 10% and precipitated calcium carbonate 10% mortars. The data was based on mortar performance for the complete test duration in all climates.

Based on the Figure 5.3 and Figure 5.4, it is evident that sorptivity coefficient values decrease when the mortars were fully carbonated. This was shown in limestone at 14-28 days and precipitated calcium carbonate at 28-42 days respectively. The trend between climates is inconclusive and is in agreement with Basheer et al. (2007) who expected this situation due to gaseous transport (carbonation) being influenced by permeability rather than sorptivity. There is a strong correlation between carbonation depth and sorptivity even though the modification formulations are varied. Overall, modified mortars show greater carbonation depths than non-modified mortar with lower sorptivity coefficients. Bai et al. (2002) explained that this attribute is due to reduced sorptivity derived from surface layer carbonation over a prolonged period of time.

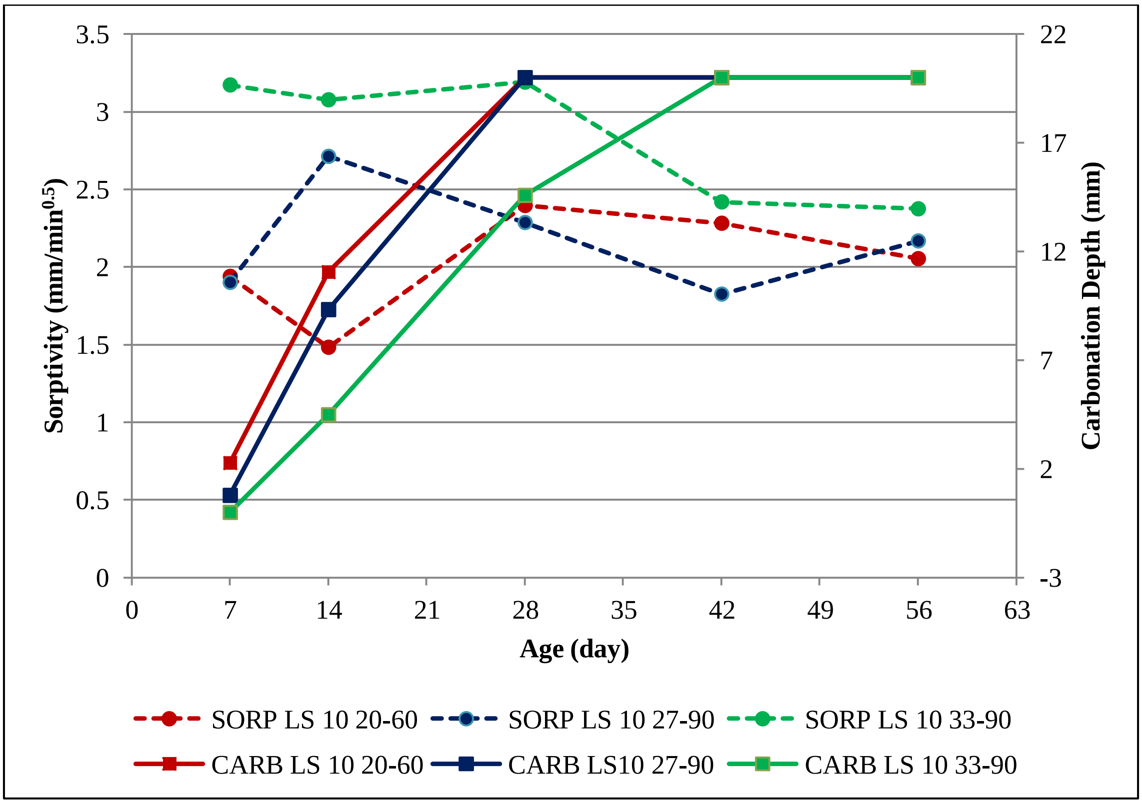


Figure 5.3: Sorptivity vs. carbonation depth of limestone mortar in all climates

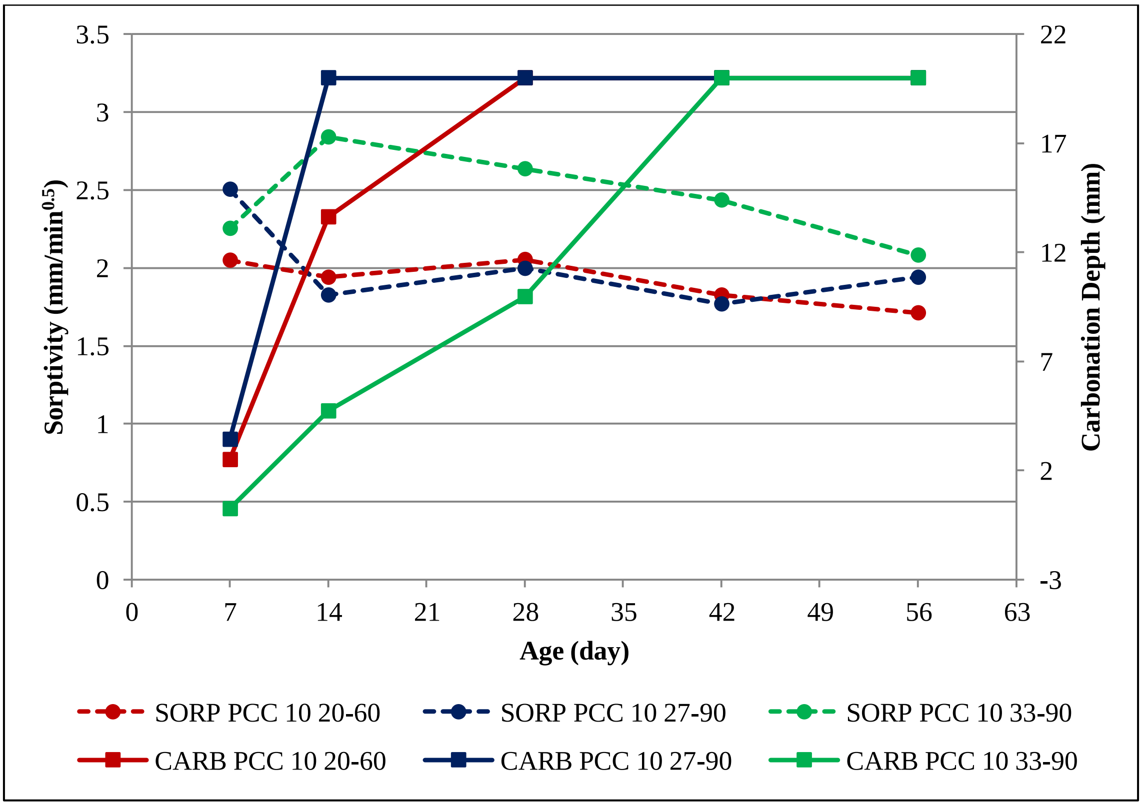


Figure 5.4: Sorptivity vs. carbonation depth of PCC mortar in all climates

Based on Figure 5.5 and Figure 5.6, the modified mortar gained in flexural strength and in concurrence with decreasing sorptivity coefficient even though PCC10 showing anomalous results. In Figure 5.7 and Figure 5.8, specimens with a lower sorptivity coefficient yielded higher flexural and compressive strength after 28 days of curing. In this study, the fineness of filler was important for the modification of aggregates-mortar interface zone which is the weakest component in the mortar (Tasdemir 2003). This small particle size filler can inhabit the voids within the binder / aggregate matrix causing the pore structures to become denser. This increases the strength but lowers the sorptivity value. O'Farrell et al. (2001) however believes that the presence of filler does not have an effect on the water absorption of mortar. The sorptivity, however, is affected significantly by not only the presence of admixture but also by composition. It can be concluded that (i) specimens with lower sorptivity coefficient will have higher tensile strength than those with greater corresponding values (Alsheikh 2013, Deb et al. 2013) and (ii) specimens with lower sorptivity coefficient will have higher compressive strength than those with greater corresponding values (Tokchom et al. 2009, Pitroda and Umrigar 2013).

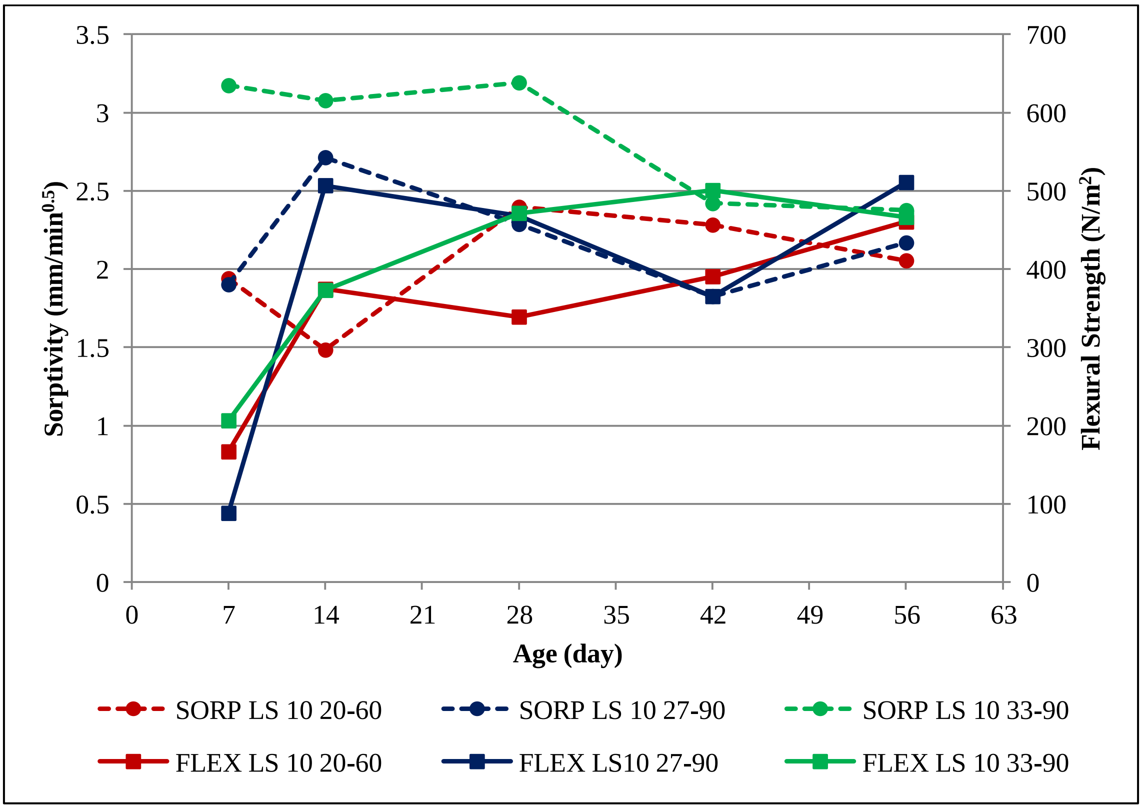


Figure 5.5: Sorptivity vs. flexural strength of limestone mortar in all climates

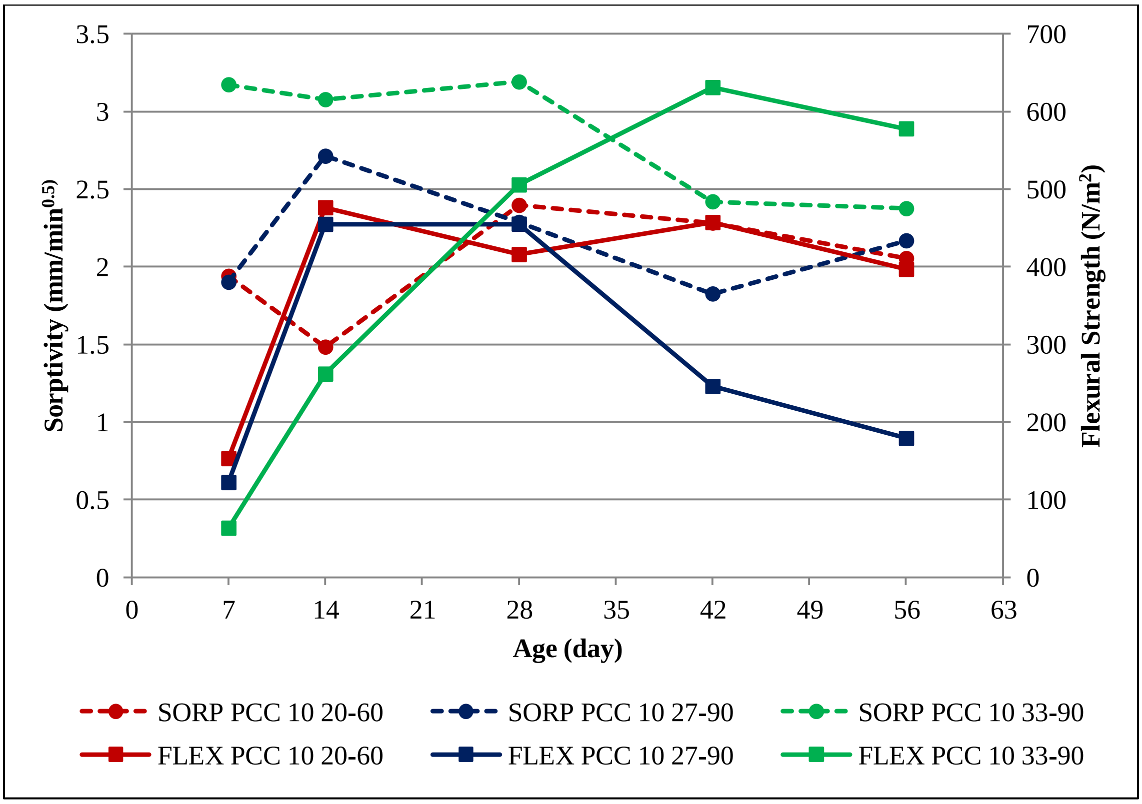


Figure 5.6: Sorptivity vs. flexural strength of PCC mortar in all climates

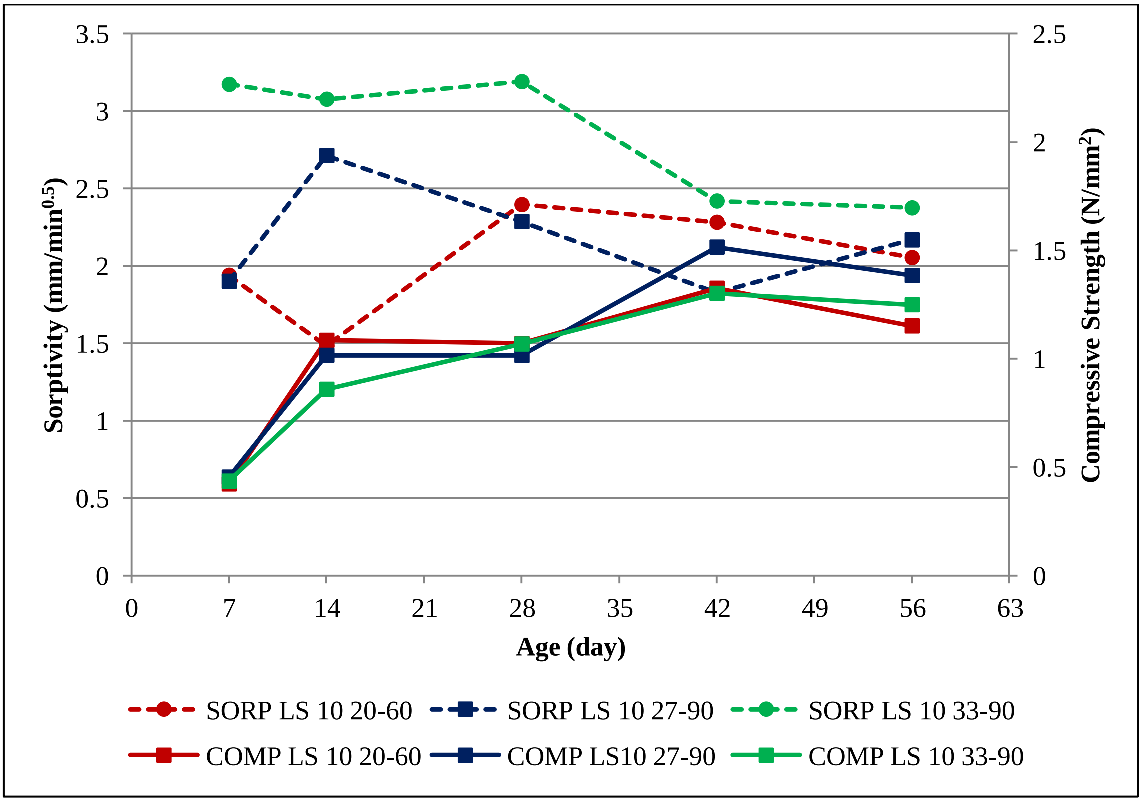


Figure 5.7: Sorptivity vs. compressive strength of limestone mortar in all climates

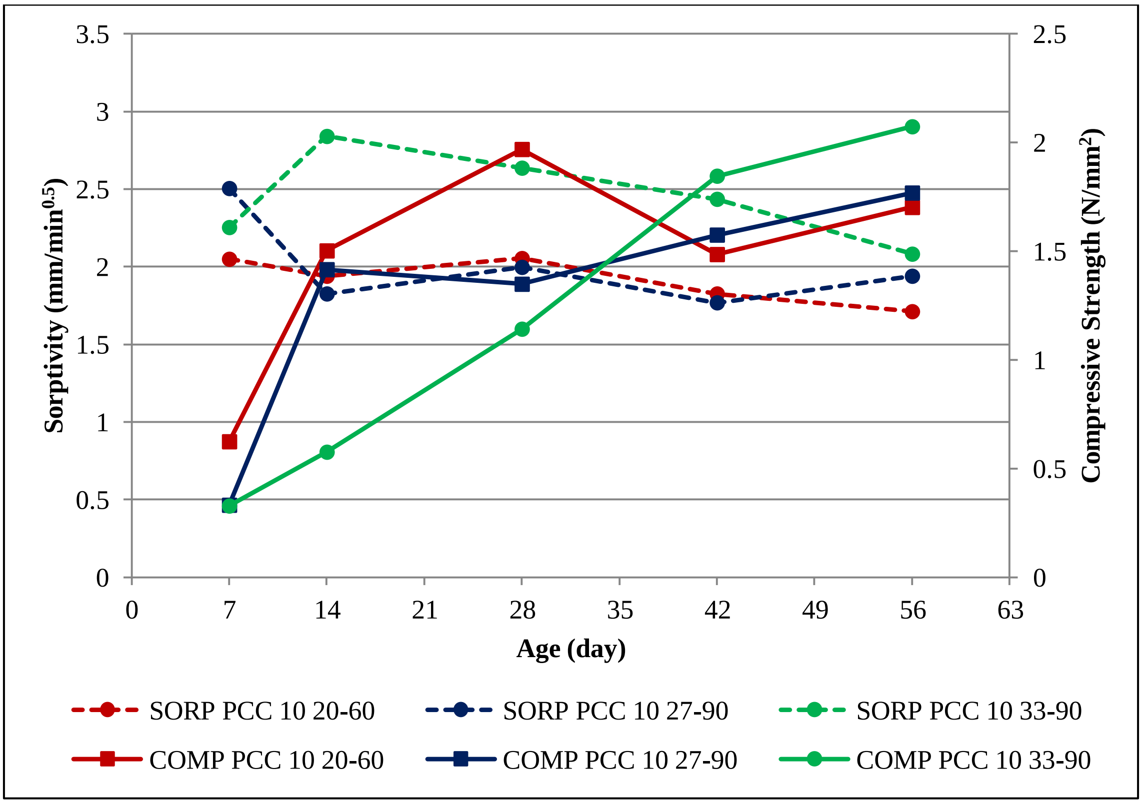


Figure 5.8: Sorptivity vs. compressive strength of PCC mortar in all climates

5.9.4 Bulk Density

A materials density relates to the atomic arrangement and the characteristics of the porous structure. This is because bulk density is directly related to the space filling and characteristics of the porous structure. According to Borges (2013), bulk density of the mortar increases with time (as carbonation progresses). In this study, the densities of all lime mortars (modified and un-modified) were not significantly different to each other; on average of 1630 - 1960 kg/m^3.

Aggregates density varies based on the type of material. For this work the bulk density of the mortar was influenced by the calcitic material substituted in the mortar affecting the grading. A lower density material produces a lower density mortar and vice versa. This is due to an aggregates bulk density affecting the mix which is batched by weight.

The precipitated calcium carbonate 10% (PCC10) has the lowest bulk density (700 kg/m^3) (see Table 3.5) compared to the other specimens. Other calcitic fillers have densities similar to Cloddach sands (variations of >17%). These findings are comparable with Checova (2009) who also found the similar results in which the bulk density of the mortar were influenced by an additives' bulk density.

This result suggested that precipitated calcium carbonate has developed a less dense structure. Therefore it results in a high porosity, low strength mortar. This finding contradicts the broad set of results for the precipitated calcium carbonates performance. This was also not reflected in the microscopy analysis. In addition, the control (un-modified) mortar in which has the lowest strength has the highest density. It can be concluded from this finding is that the bulk density hypothesis is not applicable to seeded mortars. This may be due to the chemical changes and porosity development that may have been significantly altered the calcitic materials.

5.10 Evaluating Micro-Structural Changes adopting Scanning Electron Microscopy (SEM)

The discussion of micro–structural changes can be divided into three major sub-sets; i) crystalline formation; ii) interfacial contact; and iii) materials’ purity and seeding materials’ homogeneity.

5.10.1 Crystalline Formations

Clusters of needle-like (acicular) crystals and hexagonal plate-like crystals are embedded locally within the set matrix. The needle-like (acicular) crystals are typical features of C-S-H morphology. The formation of ettringite also was identified. Ettringite is normally present in a number of hydraulic limes. Ettringite hydrates rapidly, leading to early strength development and generates a great deal of heat through its hydration reaction. Its formation would go some way to explain the strength results that all mortars cured in high temperature and humidity environments (i.e. gaining rapid strength development but subsequently experienced a strength loss after 14 or 28 days).

Use of seeding materials led to differences in the microstructure of the mortars. In the modified mortars, inter-connected agglomerations and quasi-fibrous C-S-H phases filled the pores of the mortar. Needle-like C-S-H phases were not readily observed in the matrix of these mortars. As the curing time increased, clusters of hexagonal plate-like crystals embedded locally within the carbonated matrix were observed. Upon advanced reactivity each modified mortar exhibited agglomerations of C-S-H. These hydrated phases bridged between hydrated and un-hydrated mortar compounds with growth occurring from the grain surface towards the surrounding matrix.

Modified mortars exhibited a significantly different microstructure compared to the other materials. The matrix was rich in silica and carbonated phases and was composed of agglomerated dense phases with a large open textured pore structure. Clusters of needle-like crystals and hexagonal plate-like crystals were noted embedded locally within the carbonated matrix (see Figure 4.51).

The SEM image in Figure 5.9 shows the pore structure of mortar with 10% precipitated calcium carbonate (PCC 10) at 7 days cured in 33°C – 90% RH. XRD analysis in Section 3.2.5 (Figure 3.8) verifies precipitated calcium carbonate contains 100% calcite. However, the formation of aragonite was identified (spiky-like crystals). It is believed that the aragonite formations came from; (i) silica sand that might contained aragonite crystal precursor and (ii) the secondary product of partially crystalline precipitated calcium carbonate hydration.

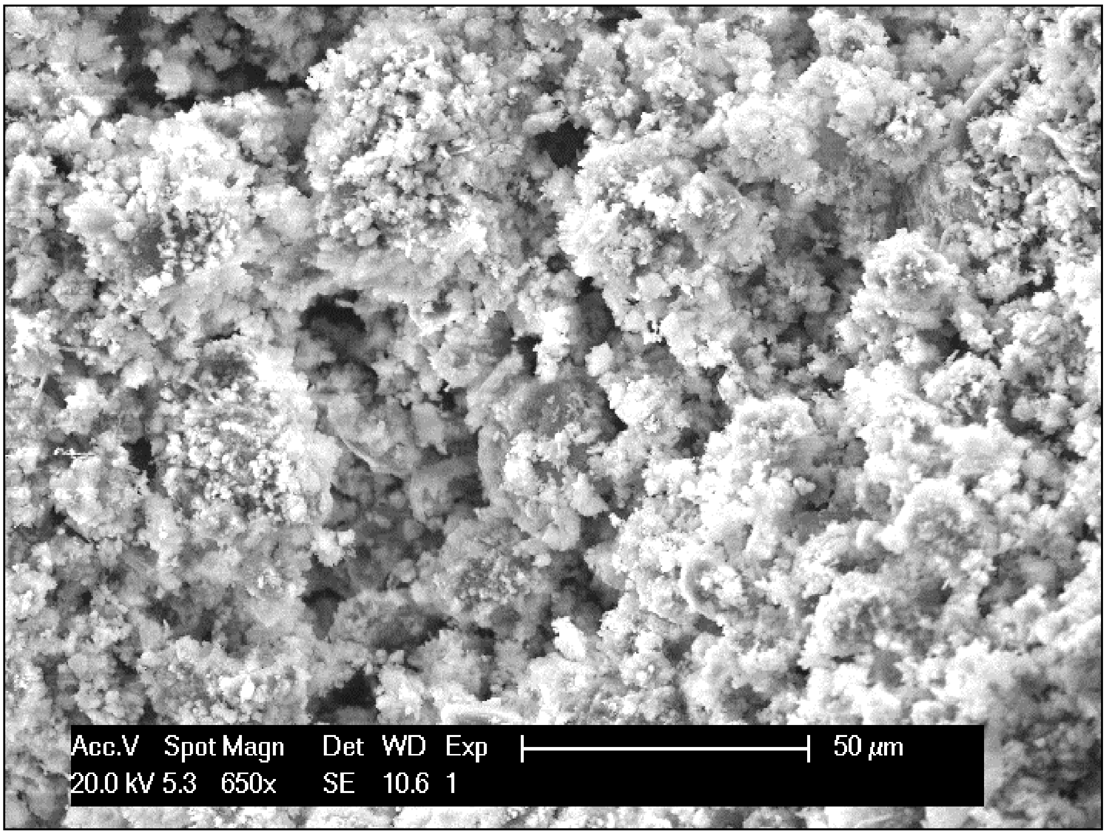


Figure 5.9: SEM image (50µm) of mortar with PCC10 at 7 days (33-90)

An increase in the volume of small pores was also observed due to the additional C-S-H phases formed by the seeding reaction. This was verified with SEM micrographs as the matrix of the calcite-mortars was mostly composed of well-connected conglomerate of

C-S-H phases with small interspersed pores. Conversely, the reference control mortar was characterized by large pores containing needle-like and reticular C-S-H phases.

5.10.2 Interfacial Transition Zone (ITZ) Between the Binder Paste and the Aggregate

Interfaces are the most important components of an amalgamated material. Characterization of the mechanical properties of interfacial zones is necessary for understanding mechanical behaviour. In this study, all modified mortar exhibit dense and uniform distribution of calcitic hexagon prisms.

It is hypothesized that mortar paste is a connected phase. The inclusion of calcitic fillers disconnected and dispersed this phase. It is now known that the structure of the mortar paste in the vicinity of the inclusions differs from that of bulk mortar paste. The region in which the presence of the inclusions affects the properties of the mortar paste is known as the Interfacial Transition Zone (ITZ) (Lutz et al. 1997). The porosity was greatest near the inclusions, and decreased with increased distance from the inclusion. In addition, the calcitic materials used are similar to the parent material (lime binder). This created a good adhesion. Limestone has the strongest positive impact on carbonation rate, of all the seeding materials. It is also the only one that can be categorically said to be 100% calcite and 100% crystalline. For this reason it provides the strongest template for the nucleation of new calcite.

However, in several mortars, various crystal formations (needle-like, plate-like, reticular and agglomerations) proved to be a disadvantage for the mortars. This is associated with the difficultly the crystals experience forming a perfect interlocking, interfacial contact. This inadequate interlocking condition can affect the mortar’s strength.

5.10.3 Purity, Particle Size and Homogeneity of Mixing

The seeding materials purity also influenced the mortars’ performance. Precipitated calcium carbonate yielded the maximum flexural and compressive strength. This can be supported by the micro-structure images, in which precipitated calcium carbonate mortars developed larger sizes of calcite platelet compared to other modified specimens at day 7.

The particle size of precipitated calcium carbonate also influenced the mortar performance. This is concurring with chemical reaction theory by Peters et al. (1996) that chemical reaction effect is greater with small particles because of increased total surface area exposed to the mixture compounds.

Homogeneity strongly influences the mortar flexural strength. It is important that in mortar modification, all the materials are properly mixed so that every part of the mortar paste has the same consistency. Non-homogeneous pastes can create particle dislocation when the mortar hardens. From the SEM images (Figure 4.32-4.55), the modified mortars have dense and uniformly distributed calcite crystals. This homogeneity creates a perfect interlocking structure between the calcite crystallites. This can contribute to beneficial strength development. It is also the reason modified mortars have lower sorptivity values than control (un-modified) mortars.

It was shown that mortars cured in elevated temperature and humidity suffered unfavourable effects which may affect the damage to the pore structure. Based on micro-structure analysis, it is evident that inclusion of calcite in the mortar gives beneficial results.

5.11 Summary - Physical Properties

From the data obtained, it can be summarized that temperature, humidity, curing time and calcitic filler influence the mortars physical characteristics. Seeding materials have been shown to increase the strength relative to the control (un-modified) mortars. The effectiveness of calcitic fillers can be evaluated based on two primary determinants; i) calcitic composition (calcium carbonate purity) and, ii) particle size. All calcitic fillers used have similar calcium carbonate form but they are differentiated by their relative purity. The second significant factor is the particle size. The performance of each modified formulation mortar was strongly influenced by the proportion and substituted materials particle size. The smaller the particle size, the more effective the seeding material (Peters et al. 1996).

The sorptivity test analysed water absorption though mortar capillaries to investigate pore structure. The water absorption graphs of all modified mortars conformed to a straight line (Figure 4.23 – Figure 4.25). This validates the performance of the specimens in all climates with the exception of certain anomalies. This illustrates that the sorptivity increases with amount of evaporated water in the mortar and is influenced by the connectivity of the pore network.

Micro-structural analysis was important to validate the results obtained earlier. The SEM images provide information on physical and chemical properties of individual micro scale systems. Based on the findings, it can be summarized that modified mortars produced large and inter-connected calcite prisms that enhance the mortars performance.

5.12 Other Factors Influencing the Modified Mortars Performances

Apart from the seven major parameters utilised evaluate the mortar's performance there are two other parameters to be considered; water/lime (W/B) ratio and curing condition.

5.12.1 Water/binder (W/B) Ratio

The water:binder ratio of 1:6 and binder:sand of 1:3 were kept constant in all modified mortar formulations This water:binder ratio was slightly higher than the recommended ratio (1:4) that had been utilised by Allen et al. (2003). During the manufacture of the samples a water/binder ratio of 1.4 was found to be unsuitable due to the influence of calcitic aggregates in the mortars. A ratio of 1.6 was utilised as it enabled conformity to the flow table testing (regression, R^2= 0.99889).

Clearly, the water ratios are a critical factor as the mortar requires sufficient water to fully hydrate water yields a higher proportion of pores. Thus the greater the water/binder ratio above the minimum required for complete hydration, the greater the amount of capillary pores created and therefore the higher the porosity of the hardened paste. The higher water/binder ratio used in this study, did not adversely affect the performance of the mortar produced. Winnefeld and Böttger (2006) presented data which show that increased water content in air lime mortars does not reduce compressive strength. It has been shown that higher porosity in air lime mortars allows greater access to atmospheric carbon dioxide, which promotes carbonation and enhances rapid early compressive strengths (Lanas and Alvarez-Galindo 2006).

From observation using this water/binder ratio, it is verified that the ratio is compatible with the mortar to be produced. This is because the mortar was mechanically compacted and the calcitic filler absorbed more water for hydration. In addition, mechanical strength test results do not show significant deviation from accepted wisdom.

5.12.2 Curing Time

The mixing formulation (water:binder ratio) and proportions has an effect on durability of mortar (Allen and Iano 2009). The integral role that water plays in hydration and the formation of the products of hydration cannot be understated. If rapid water loss occurs then insufficient water for hydration will occur and partial hydration will result. Curing conditions, also affect the mortar carbonation process. The duration for curing time depends on lime content, and must be adjusted to mortar design (in this study 56 days strength) and environmental conditions. In elevated climates such as 27°C - 90% RH and 33°C - 90% RH, the hydration is greatly accelerated. Generally, after 7 days, the strength of mortars increased rapidly after which it reduced and the strength approaching its long term value.

5.13 Reviews on Findings

Aggregates and their properties are an essential factor in determining the mechanical strength of a mortar. Previously, researchers used natural aggregates with calcareous characteristics to substitute binder for cost-effective high strength mortar. This can be seen in works by Yoon et al. (2003), Yoon et al. (2004), Guemmadi (2009), Yang et al. (2010) and Zhong et al. (2012). In this study, sand aggregates were substituted by calcareous aggregates.

5.13.1 Calcitic Fillers

Based on XRD analysis, the oyster shells consist of both calcite and aragonite. Unfortunately, there is no way of determining the proportion of each. The potential ‘seeding’ effect of the calcite in this material is ‘diluted’ by the presence of aragonite; as it is known to be un-reactive (Miyake et al. 1988). This correlates with the carbonation results in which oyster shells have virtually no effect (compared to the control) on carbonation.

Contrary to expectations, modified mortar with precipitated calcium carbonate in 33°C – 90% RH took 42 days to fully carbonate in contrast to 20°C – 60% RH and 27°C – 90% RH (28 days and 14 days respectively). It is not fully understood why the precipitated calcium carbonate has very little impact on carbonation in 33°C – 90% RH (see Figure 4.13). The fact that XRD analysis showed this to be calcite indicates that it is a crystalline material and therefore should be capable of acting as a seed. It has little impact on carbonation compared to the control. It is believed that factors influencing this are, (i) the proportion of the precipitated calcium carbonate that is crystalline (it was considered to be amorphous even though there was no evident amorphous content from the shape of the diffractogram) or (ii) because all the material is only semi-crystalline, therefore reducing the seeding ability of the precipitated calcium carbonate. It is suggested that calcite actually crystallises from an amorphous precursor; amorphous calcium carbonate (ACC). Amongst the natural calcite, limestone has the strongest positive impact on carbonation rate– it is also the only one that we can be sure is 100% calcite and 100% crystalline – therefore providing the strongest template for new calcite nucleation.

The most successful seeding carbonates yield the strongest compressive strength and have the lowest sorptivity. Figure 5.10 and 5.11 illustrate the performance of limestone and precipitated calcium carbonate as the best seeding materials. These radar diagrams are a helpful way of presenting the performance of nine formulations (including control) and six parameters; pH, moisture loss (%), carbonation rate (mm), flexural strength (N/m^2), compressive strength (N/mm^2) and sorptivity (mm/min$^{0.5}$). Note that the scales are not easily compared for pH and carbonation but are meaningful for the other parameters.

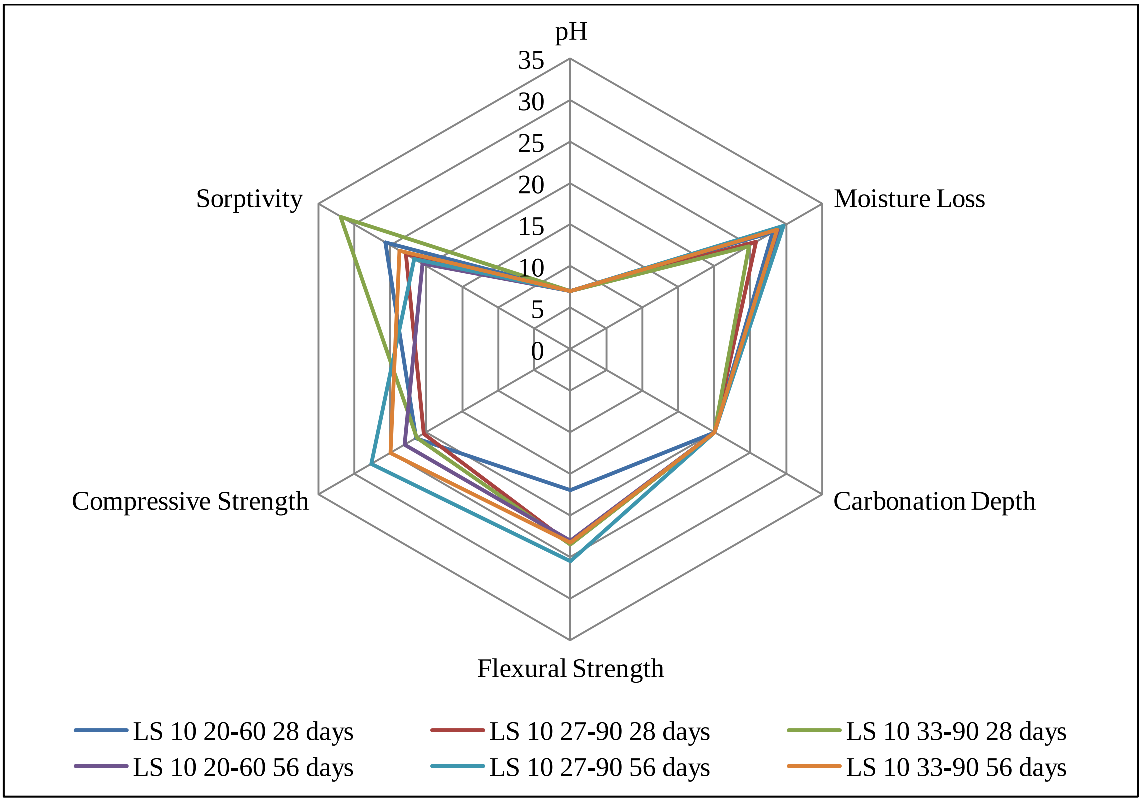


Figure 5.10 Overall performance of limestone at 28 and 56 days in all climates

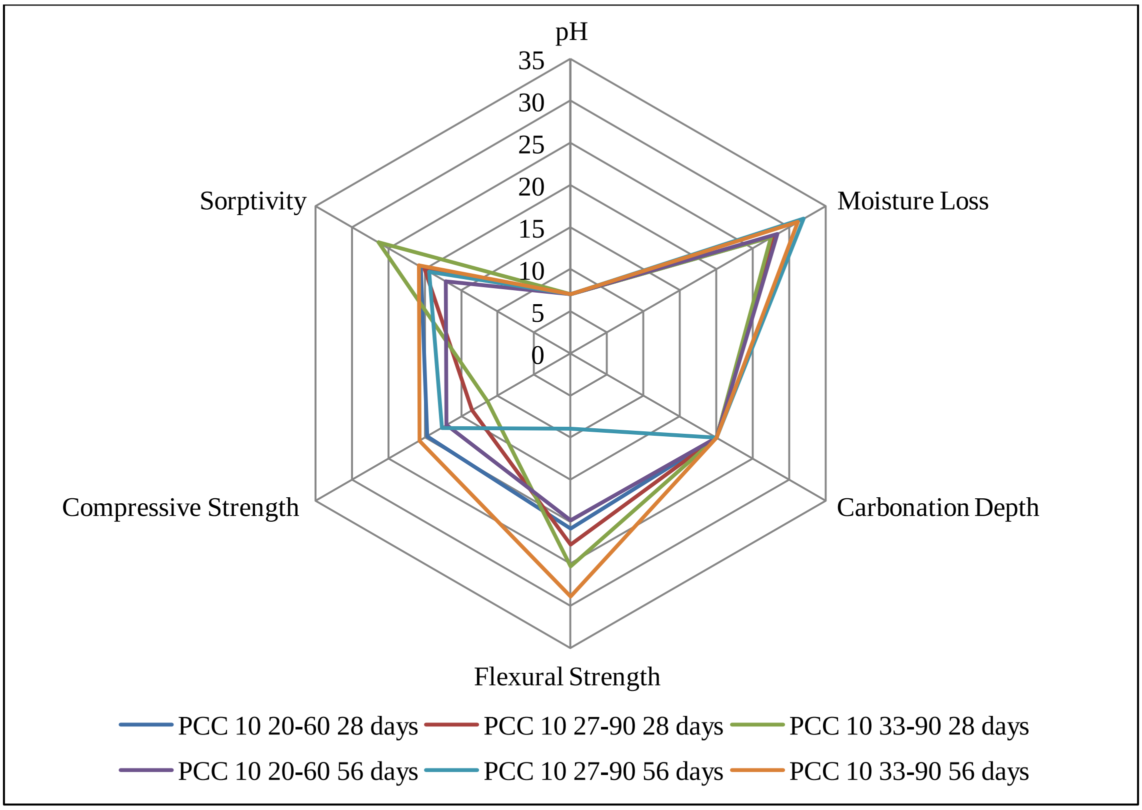


Figure 5.11: Overall performance of PCC at 28 and 56 days in all climates

5.13.2 Climates

Figure 5.12, 5.13 and 5.14 illustrate overall performance of all mortars at 56 days for all curing climates. These radar diagrams present the performance of nine formulations (including control) and six parameters; pH, moisture loss (%), carbonation rate (mm), flexural strength (N/m^2), compressive strength (N/mm^2) and sorptivity ($mm/min^{0.5}$). General, all mortars show a similar performance tendencies in all climates. Certain exceptions will be discussed fully.

There is no significant differences between all modified mortars in pH, moisture loss and carbonation depth. However, there are significant results in flexural strength, compressive strength and sorptivity coefficient especially for mortars modified by limestone powder and precipitated calcium carbonate.

Taking into account of previous discussion and Figure 5.12, the evidence from this study suggests that seeding is ineffective practice at 20°C – 60% RH climate. However, the significance of seeding in high temperature and humidity climates are clearly supported by the findings summarized in Figure 5.13 and Figure 5.14. Overall, the curing environment is important in the development of the mortars microstructure. This study has shown that seeding is effective for mortars cured at elevated temperature and humidity. The findings of this study suggest that modified mortars through seeding can increased the mortar performance especially carbonation rate, flexural strength, compressive strength and sorptivity.

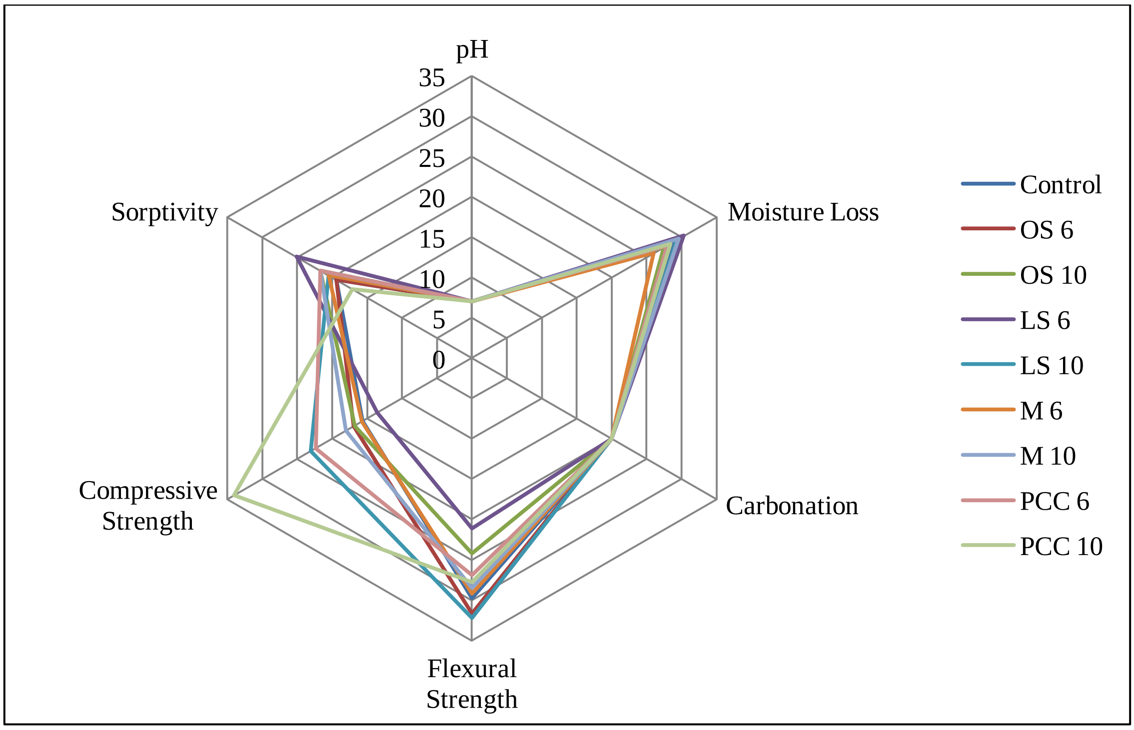


Figure 5.12: Overall performance of all mortars at 56 days in 20°C – 60% RH

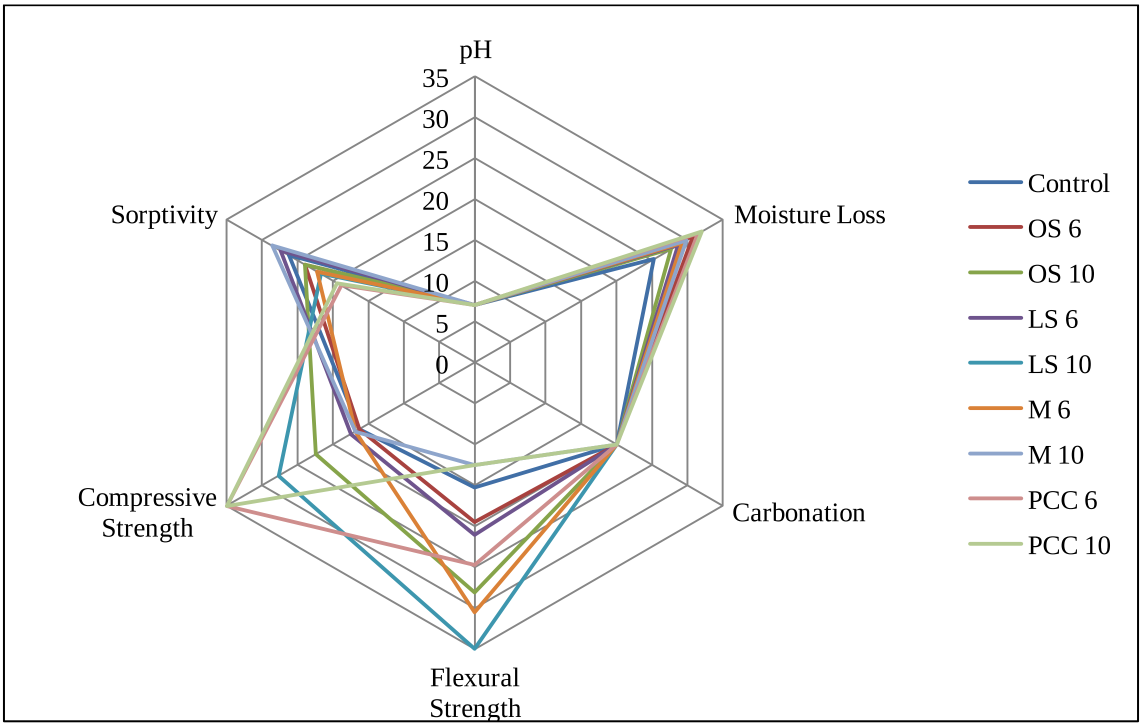


Figure 5.13: Overall performance of all mortars at 56 days in 27°C – 90% RH

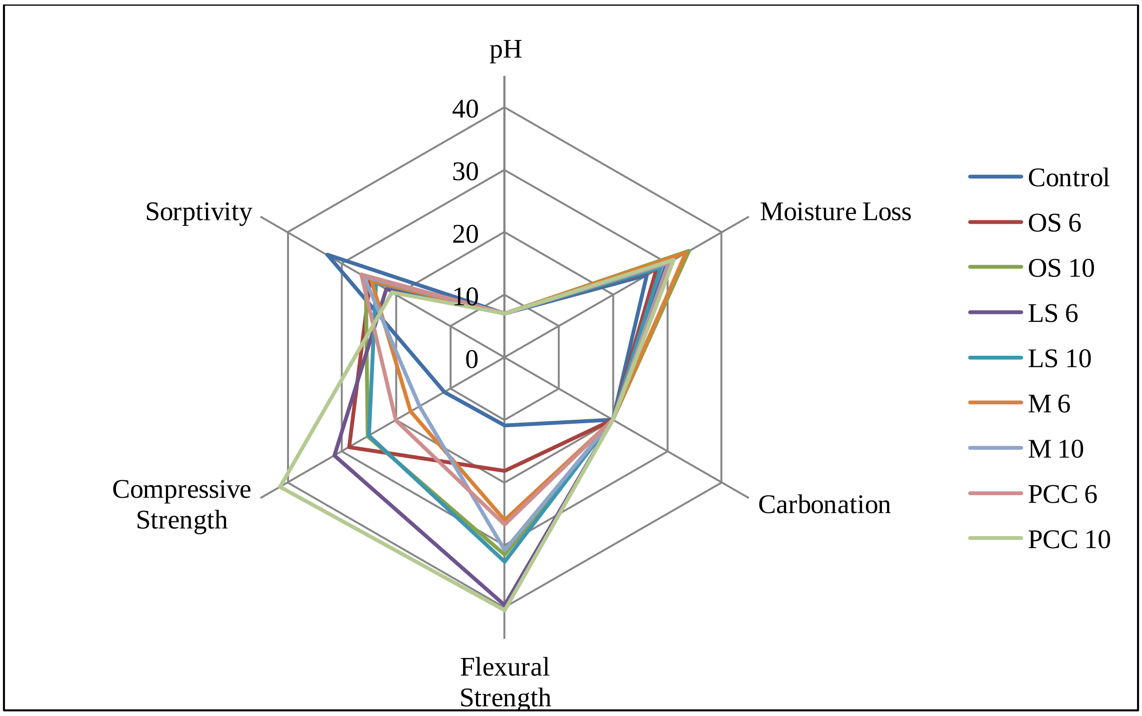


Figure 5.14: Overall performance of all mortars at 56 days in 33°C – 90% RH

CHAPTER 6

CONCLUSION

6.1 Major Conclusion

The conclusion on the investigation of the effects of calcitic fillers on modified Natural Hydraulic Lime (NHL) mortars are presented in this chapter. This study was carried out to investigate the effects of natural hydraulic lime mortars subjected to high temperature and humidity environments and investigated the subsequent effect of calcium carbonate ($CaCO_3$) modification on early development of various chemical and physical properties of the material. Primary mortar parameters such as moisture loss, pH, carbonation depth, flexural and compressive strength, sorptivity and microscopy analysis (SEM) were studied. The conclusion presented here are a reassertion of those objectives outlined in Chapter 1. The five objectives and the over-arching findings are;

Objective 1: to investigate the effects of hydraulic lime mortar performance exposed to high temperature and humidity during curing

Mortars cured in high temperature and humidity attained greater early-age strength but eventually resulted in lower long term strength development. It was positively proven that the seeding technique can increase the mortar performance on chemical and physical properties at high temperature and humidity conditions especially in the materials initial and early use.

Mortars modified with calcitic fillers were found to have higher carbonation rate compared to non-modified mortars. This is due to the fact that fine calcitic fillers acted as a precipitation site for the nucleation of calcite. Additionally it is believed that the hydrated phases (i.e. belite) were enhanced due to favourable dissolution / precipitation rates. Carbonation is accelerated as a result of the decrease in the calcium hydroxide content due to their consumption through the calcitic reaction. However, in spite of the mortar modifications, temperature, water content and carbon dioxide concentration remain the most important contributing factors in determining the rate of carbonation.

Objective 2: to investigate the effects of mortar seeding on chemical properties using laboratory testing techniques i.e. composition of binder

It can be summarized that from the chemical characteristics investigations;

a. Fresh mortars have higher pH values that reduce over time; attributed to progressing carbonation;

b. Modified mortars are more sensitive to curing than those without;

c. Curing at higher temperatures greatly accelerates the hydration reaction of the mortar. This appears more pronounced in those mortars with mineral inclusions;

d. These results highlight the variation in effect of seeding materials on carbonation.

Calcite filler has poor water retaining properties. This appeared to have no beneficial effects on the mortars in high temperatures. This is particularly important for mortars in hot arid environments in which it cannot be guaranteed that sufficient water is available for hydration for the important early stages. Finer calcitic filler requires additional water due to its large surface area.

It was established from the pH values attained, that a reduction in pH had taken place during carbonation. High temperature modified mortar accelerated the rate of hydration thus rapidly decreasing the value of pH due to the relatively low pH of calcite and C-S-H forms of compounds compared to $Ca(OH)_2$.

It was shown that the purity and crystallinity of the seeding materials were critical in the performance of the mortars. The higher the relative purity of the seeding material the greater the positive benefits on physical characteristics.

Objective 3: to investigate the effects of mortar seeding on physical properties using laboratory testing techniques i.e. strength

The following can be concluded from the physical characteristic investigations;

a. Experimental results indicate clear differences between the seeded specimens and the control samples with regards to the development of both flexural and compressive strength;

b. The relationships between the water absorption rates and time are valid but the gradient (sorptivity) varied with the type of calcite fillers and time. In addition, it has been shown that seeding reduces sorptivity.

It has been established that the flexural and compressive strength was influenced by porosity of the mortar. Porosity reduces the cross-sectional area across which a load is applied and acts as a stress concentrator.

It has been established that compressive strength was strongly influenced by calcitic composition (calcium carbonate content) and particle size. From the data obtained, approximately 88% of the total specimens in all climates with 10% of seeding recorded a higher flexural and compressive strength values than their 6% seeding counterpart.

Objective 4: to investigate how mortar seeding additives affect the moisture handling characteristics e.g. capillary absorption

The following can be concluded from sorptivity investigations. At 28 days, sorptivity coefficient (k), of all mortars is in range of;

i. 2.0 – 2.5 at 20°C – 60% RH;
ii. 1.6 – 3.0 at 27°C – 90% RH;
iii. 2.0 – 3.7 at 33°C – 90% RH.

It is evident that modified mortars cured in high temperature and humidity exhibited a relatively low water absorption and sorptivity. The addition of calcitic materials as aggregate substitutions, conferred better performance compared to un-modified mortars appraised through the water absorption by capillarity.

Objective 5: to investigate micro-structural changes that arises from the incorporation of mortar seeding additives through the use of ESEM analysis

The curing environment is important in the development of the mortar’s microstructure. Micro-structural changes of modified mortars were influenced by crystalline formation, interfacial contact, materials’ purity and seeding materials’ homogeneity. It is positively identified that the increase in the volume of small pores was due to the accelerated C-S-H phases formed as a consequence of the seeding reaction. However, in several mortars, various crystal formations (needle-like, plate-like, reticular and flocs-like) proved to be disadvantageous for the mortars. This is because it is difficult for the crystals to produce full and satisfactory interlocking at the interface contact between the compounds. This inadequate interlocking can reduce the mortar’s strength.

6.2 Summary

It is evident that the presence of these calcitic fillers affects both the chemical and physical performance of mortars in high humidity environments.

Three natural calcites namely; oyster shells, limestone and marble and one synthetic calcite precipitated calcium carbonated (PCC) were used adopted as calcitic fillers. At 28 days onwards, expected performance occurs in the seeding materials based upon their composition. The most successful through to the least were;

(i) Precipitated calcium carbonate (100% calcite when crystalline, but only partially crystalline);
(ii) Limestone (100% calcite, all crystalline);
(iii) (Oyster shells (>100% calcite, >0% aragonite, all crystalline);
(iv) Marble (>100% calcite, >0% aragonite, all crystalline) and;
(v) Control (no seed).

The most important feature of the success of the materials is believed to be the purity and the crystallinity of the minerals. It can be concluded that the most successful seeding materials cause the highest carbonation rate, the strongest compressive strength and have the lowest sorptivity.

In terms of over-arching findings of this work it is clear that the addition of precipitated calcium carbonate (PCC) would yield positive results in a high humidity and temperature environment. This would be most noticeable in the positive benefits in the physical characteristics. It was also shown that a 6% substitution was sufficient to increase the carbonation rate. Conversely, a higher substitution amount (10%) was required to maximize the strength development. The substitution amount did however depend on the density and particle size of the filler.

Modified mortars were proven to lessen the adverse effects of extreme climate exposure. However, modifications may not be applicable to colder climates due to the less pronounced benefits noted in the results in 20°C – 60%RH climatic condition results.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Introduction

This study has focussed on the effects of seeding in mortars cured in high temperature and humidity. During the course of the study, a number of issues were identified that would be worth future investigation.

7.2 Recommendations

It is recommended that further research be undertaken in the following areas.

7.2.1 Influence of Particle Size & ITZ Studies

It has been demonstrated that in a modified mortar, the microstructure of the interfacial transition zone (ITZ) between calcitic filler, binder and aggregates are important for strength and durability. Reactivity of calcitic filler is attributed to its high content of calcium carbonate, and to its very large surface area governed by the porous structure of the particles. However, the arguments on particle size effectiveness are not fully conclusive. A comprehensive investigation into this could be initiated to evaluate the influence of particle size of filler on carbonation depth, compressive strength and sorptivity.

7.2.2 Hydration Development & Shrinkage Cracking

It is established that all modified mortars in this study gained rapid strength in their early stages. The exothermic chemical reaction occurs during hydration which raises the temperature of mortar. The heat of hydration related to the thermal stress, and ultimately the early-age shrinkage cracking in mortars. Parameters during the hydration process, such as temperature change and the highest temperature reached during the mortar curing process are critical since they can be utilized directly to analyze the status of the future structural strength.

7.2.3 Variations of Calcitic Fillers Substitutions (proportions)

There is a need for a systematic study of the substitution quantities of the seeding materials. The amount of calcite substitution varied with the type and purpose of mortar. The arguments on substitution and its effectiveness are not fully conclusive. The performance of seeding must be further evaluated through the experimental design of density, air content, workability and compressive and tensile strength. In addition, formulations proportions must be undertaken to determine the optimum quantity.

Appendix A: Carbonation Depth

Table A.1: Carbonation depth all mortar for samples (20°C - 60% RH)

Calcitic Filler	Seeding (%)	Age (day)	Carbonation (mm)				
			Side A (top)	Side B	Side C (bottom)	Side D	Average
Control	0	7	1.31	0	0	0	0.33
		14	1.83	1.8	1.5	1.45	1.65
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Oyster shells	6	7	0	0	0	0	0.00
		14	0.4	0.5	0.44	0.45	0.45
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Oyster shells	10	7	4.6	0	0	0	1.15
		14	6.45	6	5.5	6.1	6.01
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Limestone	6	7	4.62	0	0	0	1.16
		14	6.93	6	5.2	5.8	5.98
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Limestone	10	7	9.07	0	0	0	2.27
		14	12.7	11	9.8	10.7	11.05
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Marble	6	7	4.71	0	0	0	1.18
		14	6.6	5.7	5.6	5.5	5.85
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Marble	10	7	6.42	0	0	0	1.61
		14	9.01	6	10	14	9.75
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Precipitated $CaCO_3$	6	7	10.34	0	0	0	2.59
		14	14.48	15	12.1	14	13.90
		28	20	20	20	20	20.00

		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Precipitated $CaCO_3$	10	7	10	0	0	0	2.50
		14	14.5	15	12	13	13.63
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00

Table A.2: Carbonation depth all mortar for samples (27°C - 90% RH)

Calcitic Filler	**Seeding (%)**	**Age (days)**	**Carbonation (mm)**				
			Side A (top)	**Side B**	**Side C (bottom)**	**Side D**	**Average**
Control	0	7	3.19	0	0	0	0.80
		14	20	20	20	20	20
		28	20	20	20	20	20
		42	20	20	20	20	20
		56	20	20	20	20	20
Oyster shells	6	7	3.13	0	0	0	0.78
		14	20	20	20	20	20
		28	20	20	20	20	20
		42	20	20	20	20	20
		56	20	20	20	20	20
Oyster shells	10	7	12.76	0	0	0	3.19
		14	20	13.16	8.03	13.82	13.75
		28	20	20	20	20	20
		42	20	20	20	20	20
		56	20	20	20	20	20
Limestone	6	7	0	0	0	0	0.00
		14	16.84	8.97	7.1	7.78	10.17
		28	20	20	20	20	20
		42	20	20	20	20	20
		56	20	20	20	20	20
Limestone	10	7	3.4	0	0	0	0.85
		14	13.75	9.22	7.66	8.06	9.67
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Marble	6	7	12.61	0	0	0	3.15
		14	20	20	5.49	20	16.37
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Marble	10	7	9.25	0	0	0	2.31
		14	20	20	1.73	20	15.43
		28	20	20	20	20	20.00

		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Precipitated $CaCO_3$	6	7	16.03	0	0	0	4.01
		14	20	20	20	20	20
		28	20	20	20	20	20
		42	20	20	20	20	20
		56	20	20	20	20	20
Precipitated $CaCO_3$	10	7	16	0	0	0	4.00
		14	20	20	20	20	20
		28	20	20	20	20	20
		42	20	20	20	20	20
		56	20	20	20	20	20

Table A.3: Carbonation depth all mortar for samples (33°C - 90% RH)

Calcitic Filler	Seeding (%)	Age (days)	Carbonation (mm)				
			Side A (top)	Side B	Side C (bottom)	Side D	Average
Control	0	7	1.47	0	0	0	0.37
		14	2.83	3.89	5.26	3.83	3.95
		28	6.63	7.3	7.43	7.08	7.11
		42	12.38	14.24	12.33	13.48	13.11
		56	20	20	20	20	20.00
Oyster shells	6	7	0	0	0	0	0.00
		14	4.66	4.16	4.15	3.81	4.20
		28	7.4	7.4	7.28	6.87	7.24
		42	12.75	12.45	11.32	12.05	12.14
		56	20	20	20	20	20
Oyster shells	10	7	1	0	0	0	0.25
		14	5.33	5.33	4.93	5.99	5.40
		28	14.15	12.29	11.44	12.15	12.51
		42	20	20	20	20	20
		56	20	20	20	20	20
Limestone	6	7	0	0	0	0	0
		14	3.68	5.26	4.11	5.25	4.58
		28	15	15	15	15	15.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20
Limestone	10	7	1	0	0	0	0.25
		14	5.21	5.35	4.26	5.02	4.96
		28	10.17	10.17	10.18	11.79	10.58
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Marble	6	7	0	1.4	0.94	1.3	0.91
		14	2.62	3.15	2.86	3.28	2.98
		28	20	20	20	20	20.00

		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Marble	10	7	1.73	0	0	0	0.43
		14	3.01	3.19	2.72	3.17	3.02
		28	20	20	20	20	20.00
		42	20	20	20	20	20.00
		56	20	20	20	20	20.00
Precipitated $CaCO_3$	6	7	0.72	1.6	2.77	1.38	1.62
		14	4.42	4.5	4.45	4.36	4.43
		28	9.14	9.83	9.43	9.32	9.43
		42	13.4	13.98	12.93	13.72	13.51
		56	20	20	20	20	20
Precipitated $CaCO_3$	10	7	1	0	0	0	0.25
		14	5.21	5.35	4.26	5.02	4.96
		28	10.17	10.17	10.18	11.79	10.58
		42	20	20	20	20	20
		56	20	20	20	20	20

Appendix B: Environmental Scanning Electron Microscopy (SEM) Images of Lime Mortars

These are the images from the discussion in Section 4.10 Microscopy Analysis by Environmental Scanning Electron Microscopy (ESEM).

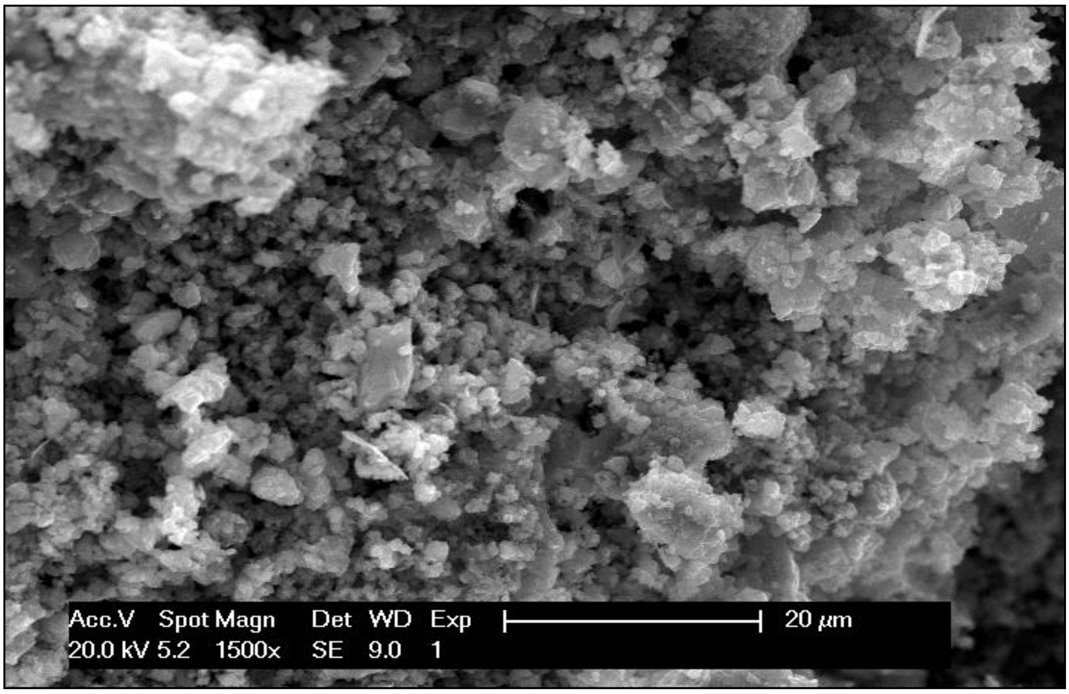


Figure B.1: SEM image of control specimen at 7 days (20-60)

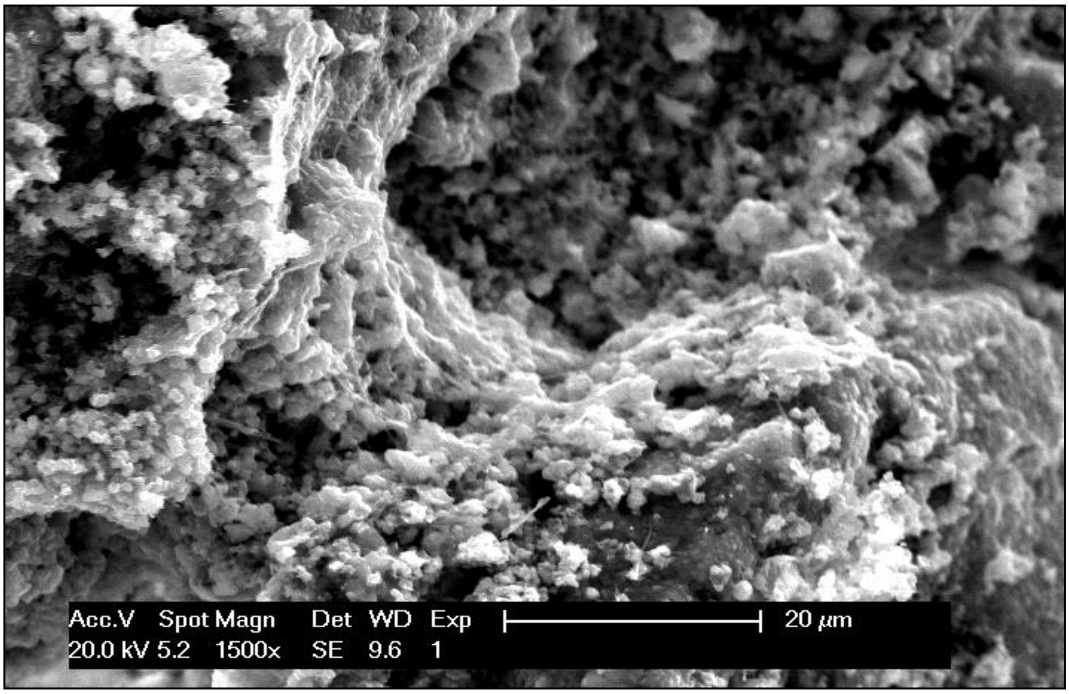


Figure B.2: SEM image of control specimen at 28 days (20-60)

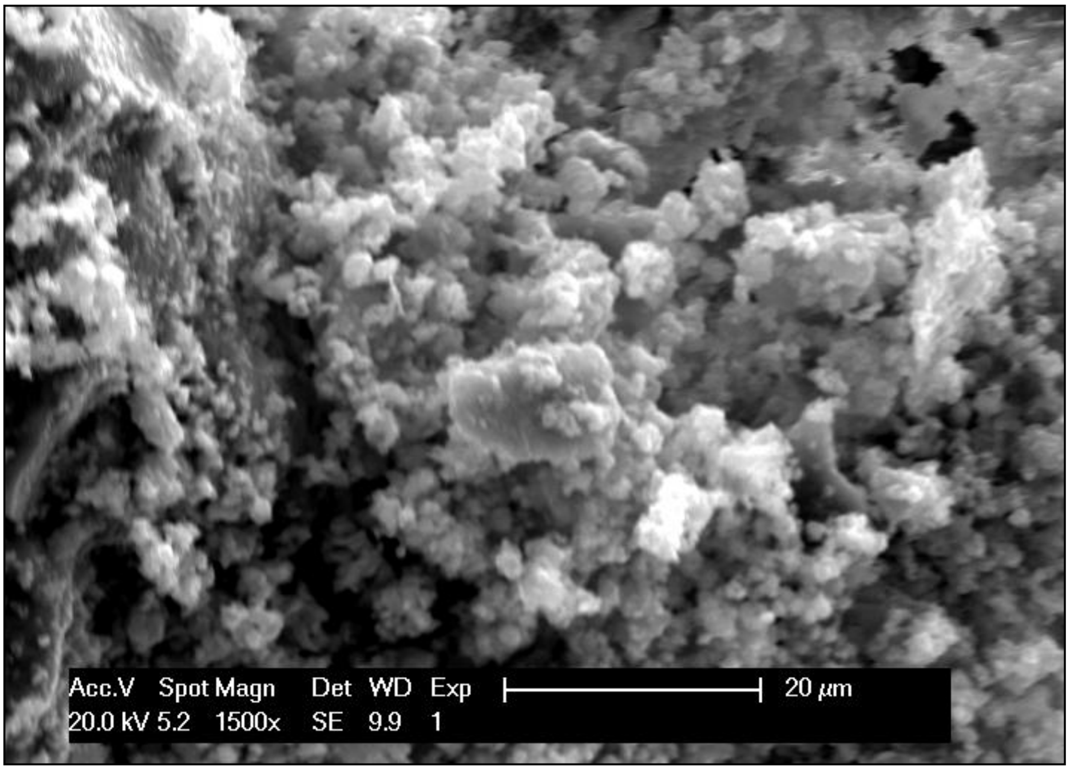


Figure B.3: SEM image of control specimen at 56 days (20-60)

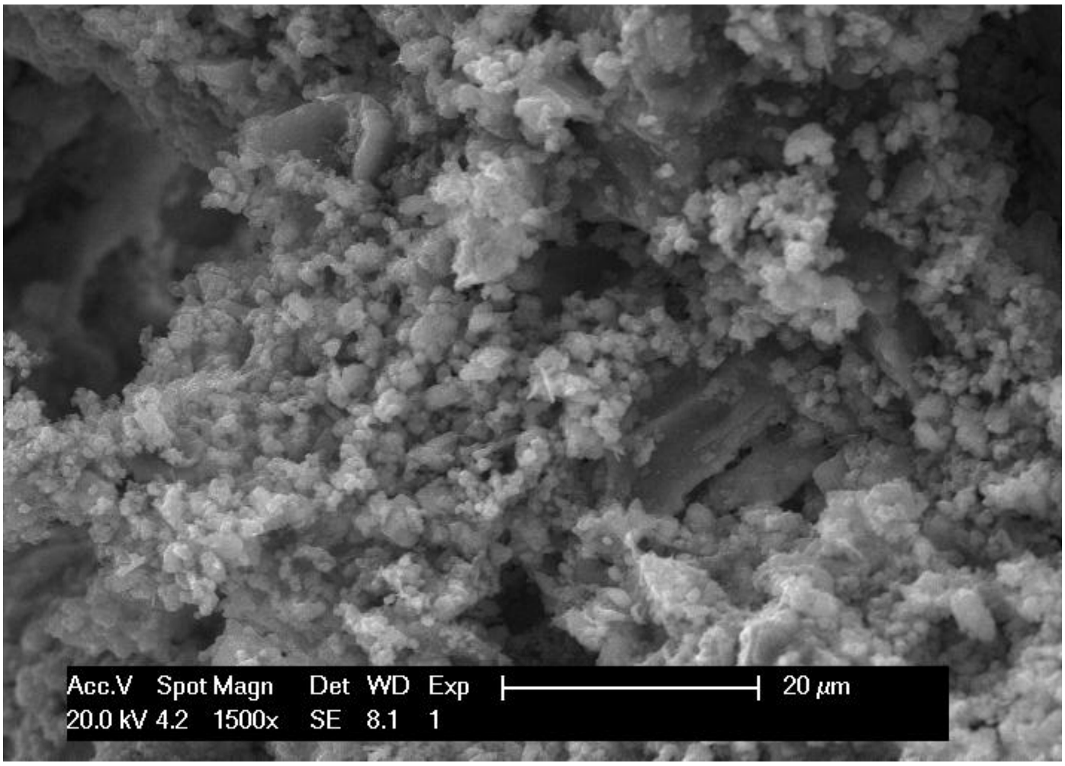


Figure B.4: SEM image of mortar with 6% of oyster shells at 7 days (20-60)

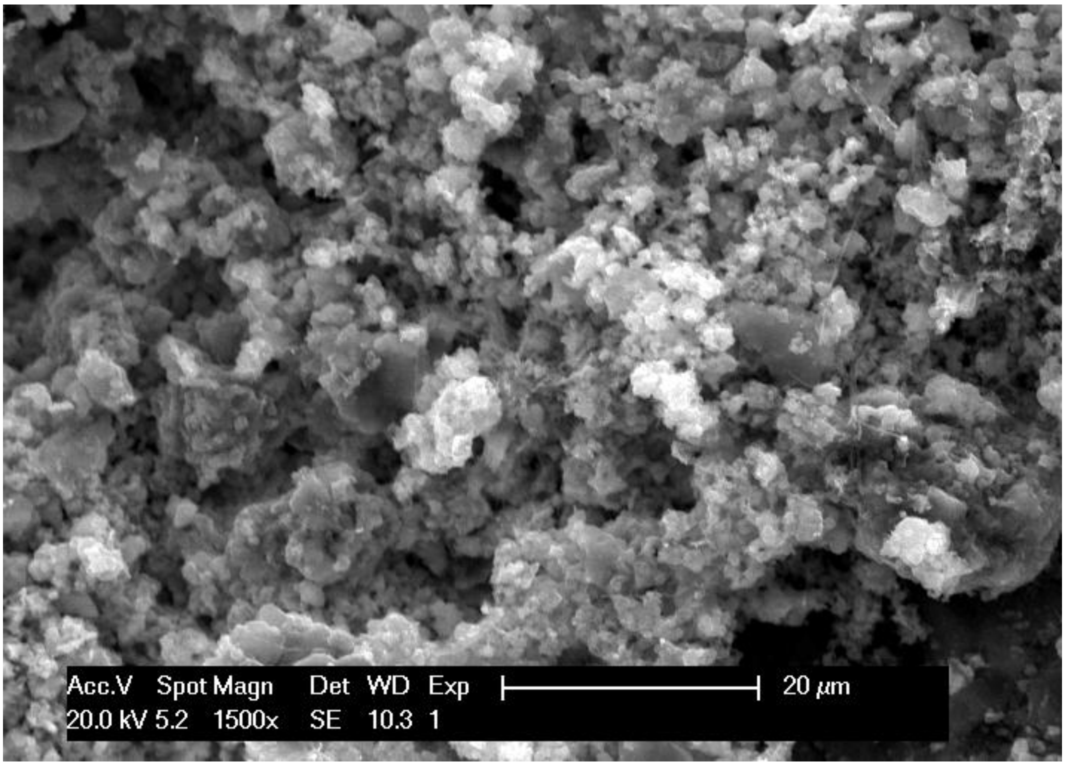


Figure B.5: SEM image of mortar with 6% oyster shells at 28 days (20-60)

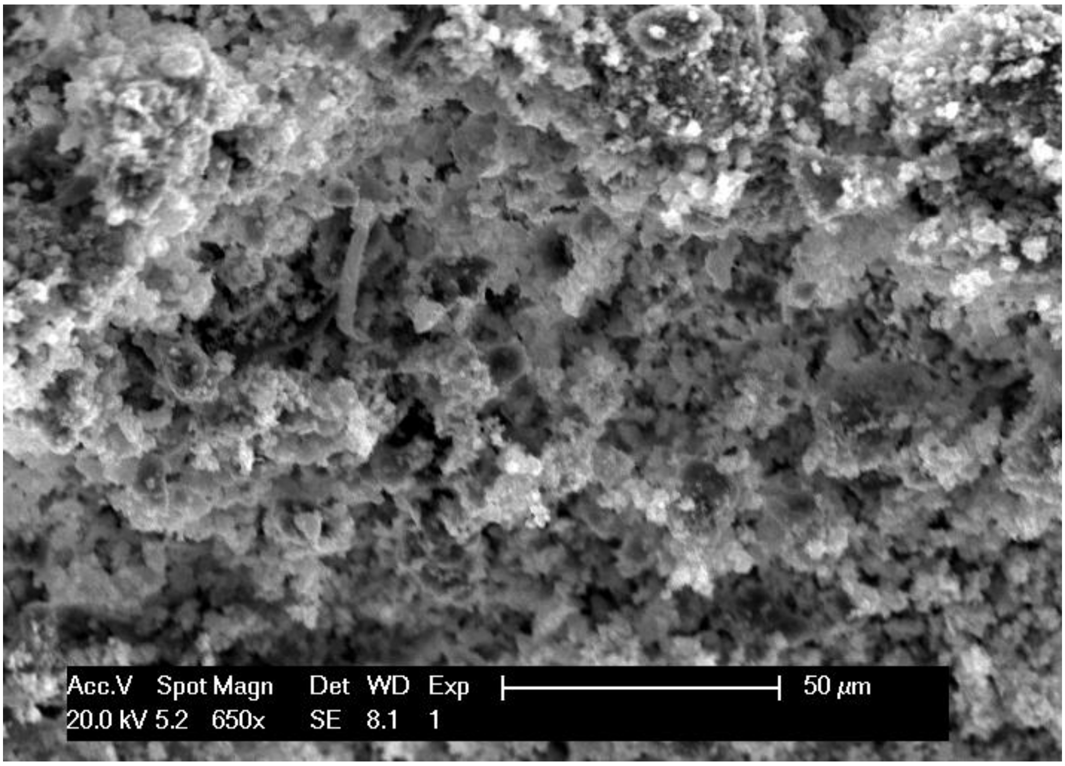


Figure B.6: SEM image of mortar with 6% oyster shells at 56 days (20-60)

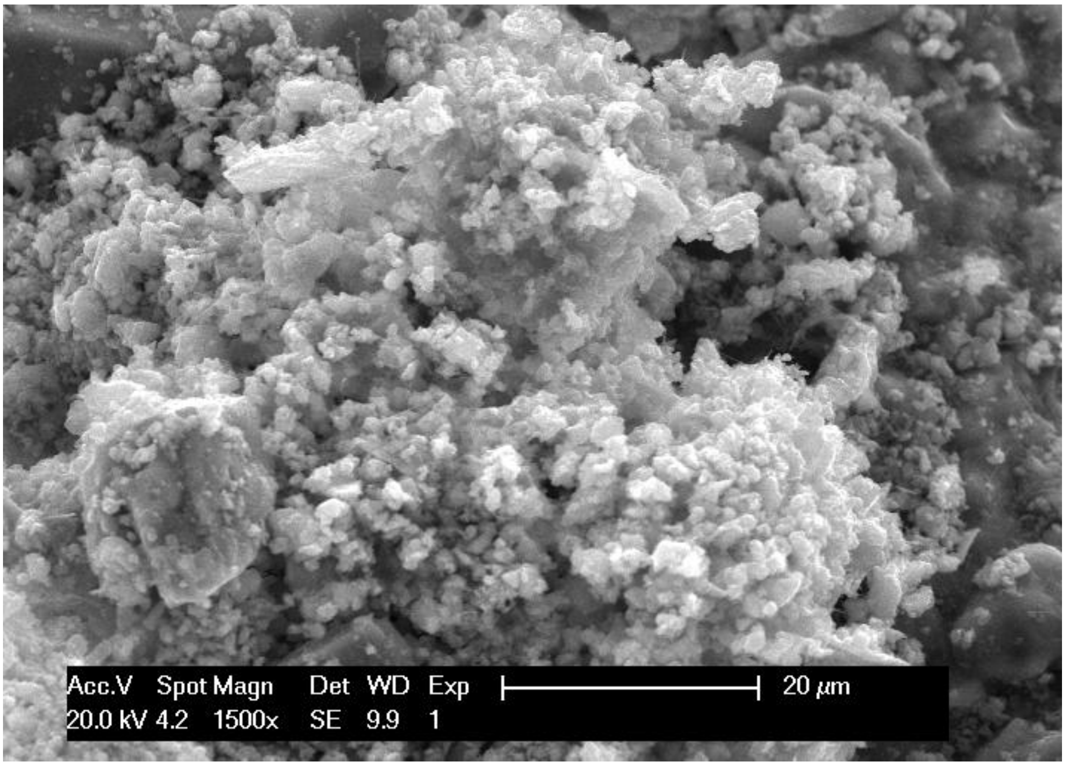


Figure B.7: SEM image of mortar with 10% oyster shells at 7 days (20-60)

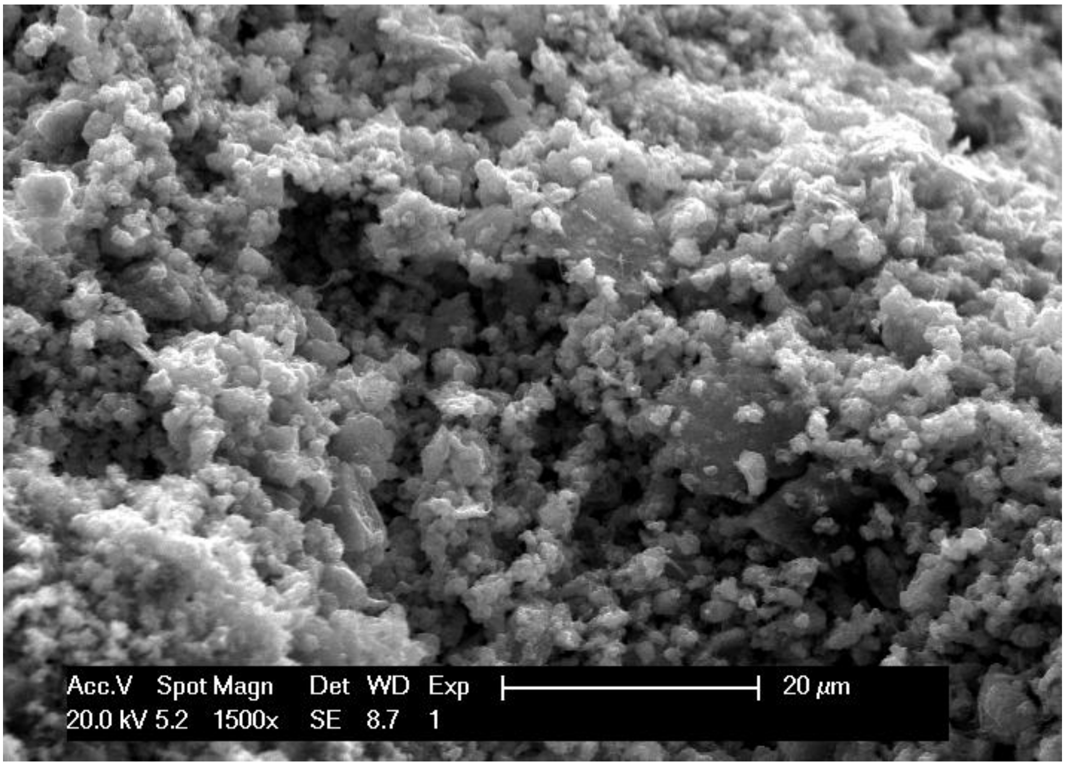


Figure B.8: SEM image of mortar with 10% oyster shells at 28 days (20-60)

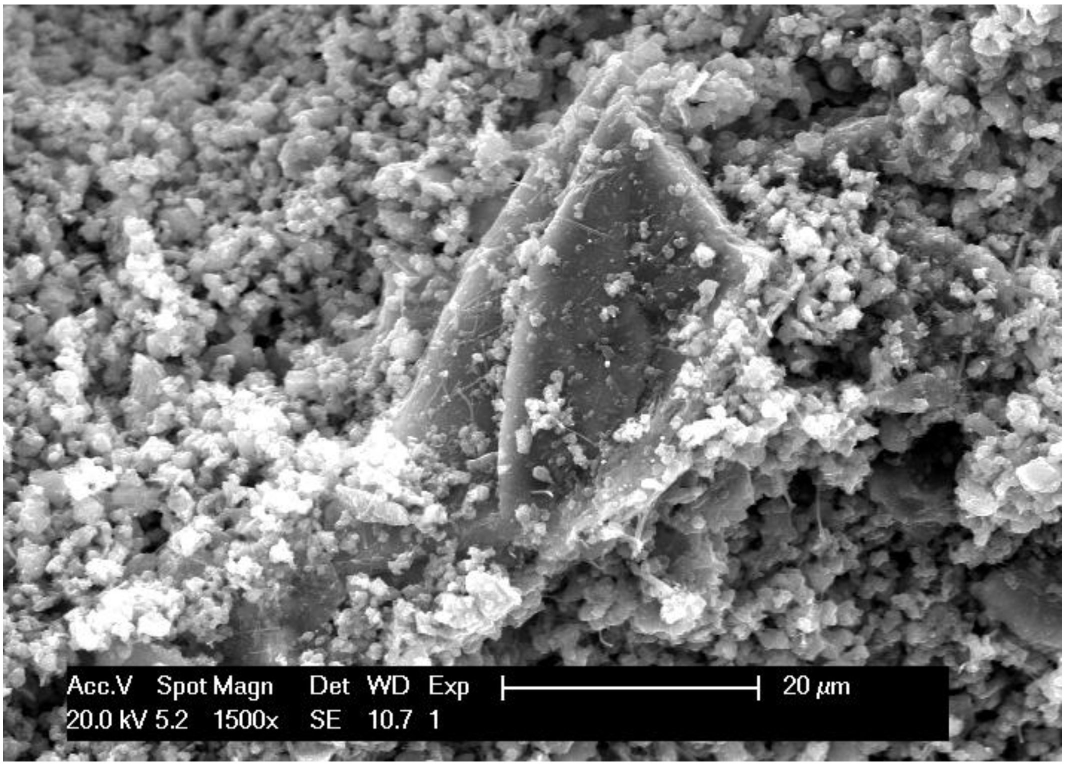


Figure B.9: SEM image of mortar with 10% oyster shells at 56 days (20-60)

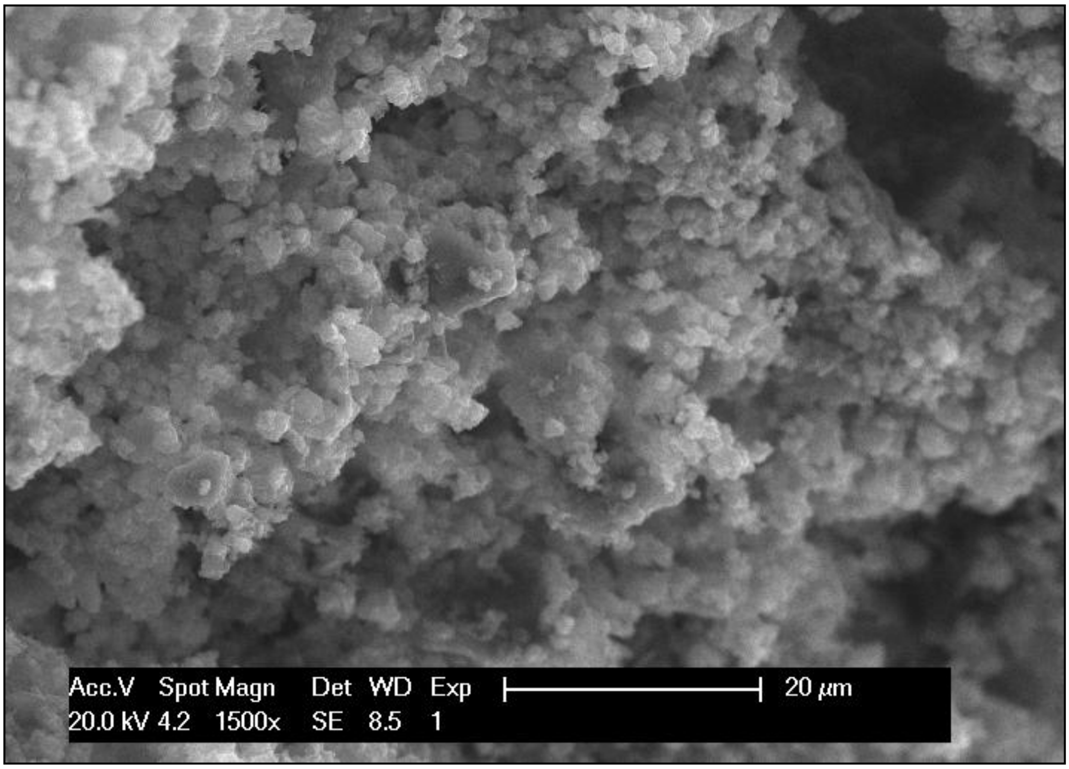


Figure B.10: SEM image of mortar with 6% limestone at 7 days (20-60)

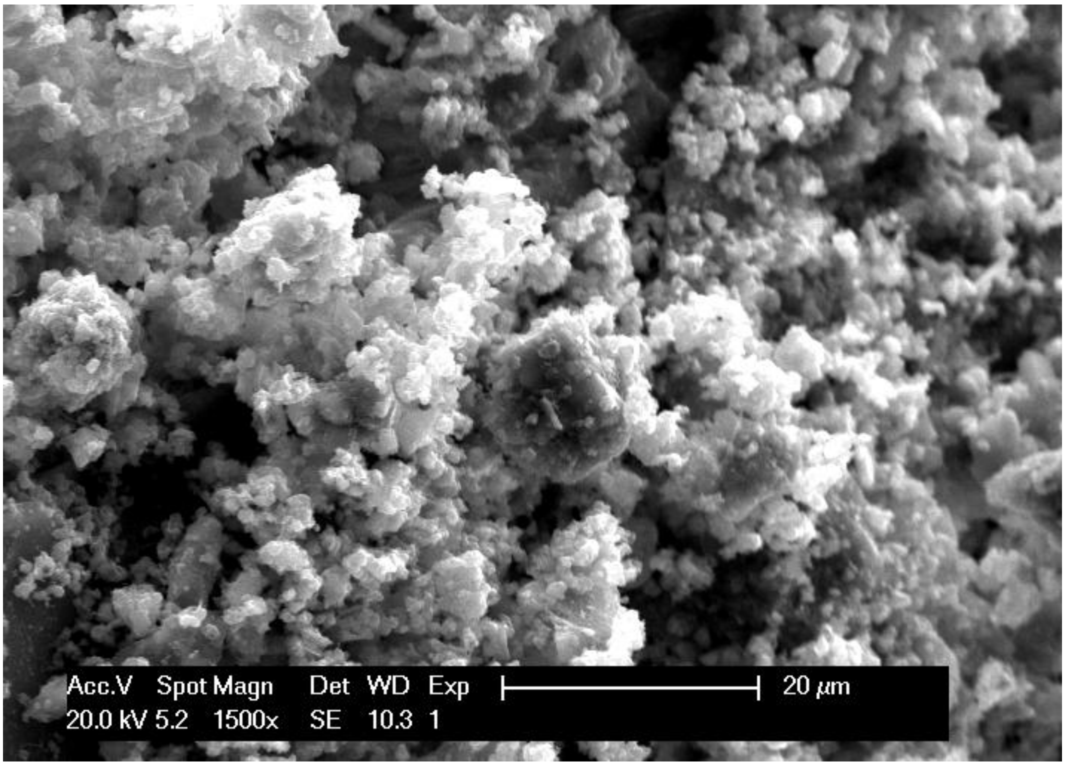


Figure B.11: SEM image of mortar with 6% limestone at 28 days (20-60)

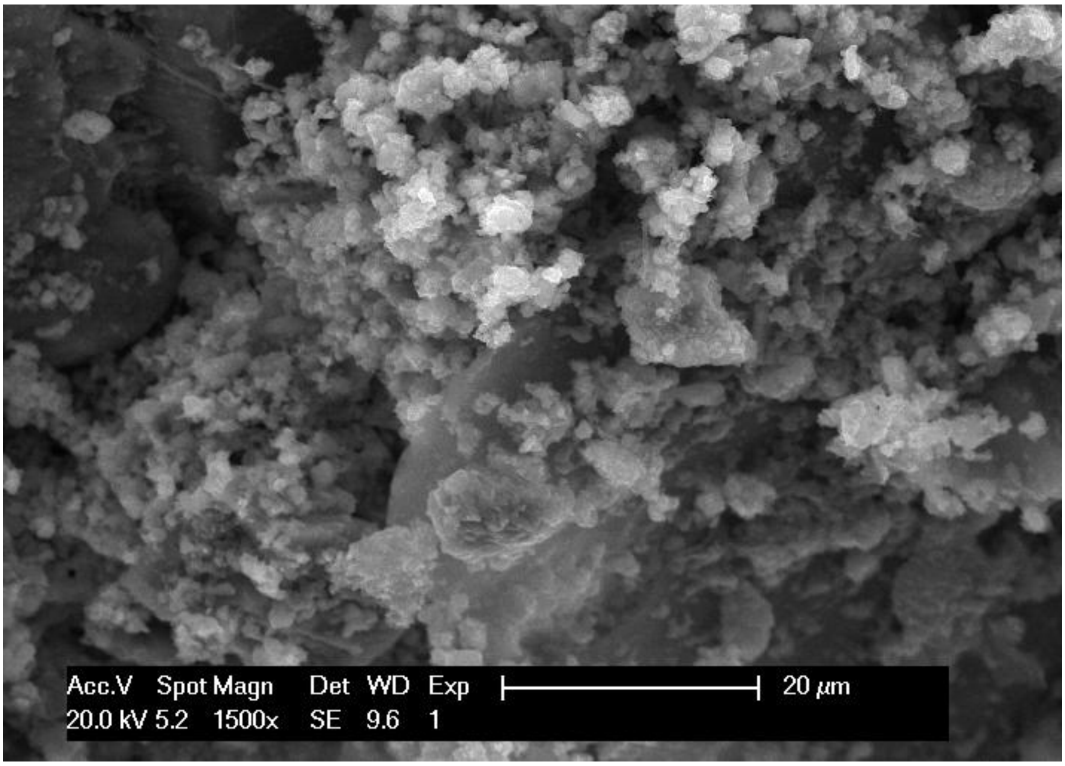


Figure B.12: SEM image of mortar with 6% limestone at 56 days (20-60)

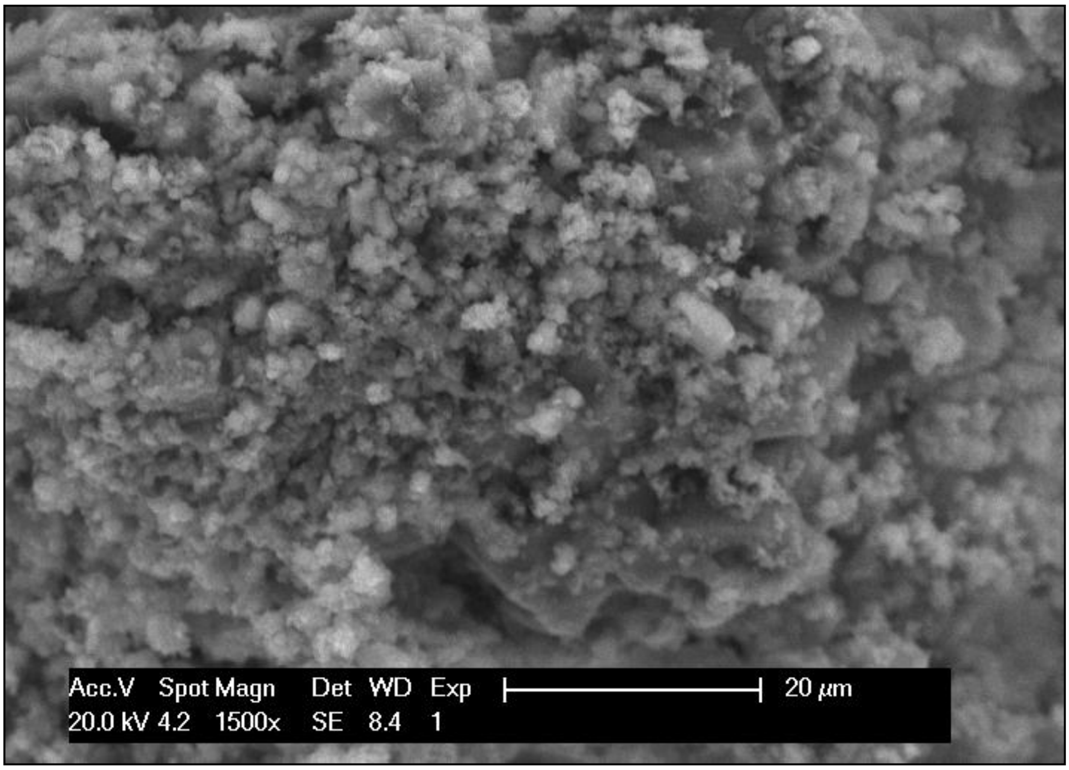


Figure B.13: SEM image of mortar with 10% limestone at 7 days (20-60)

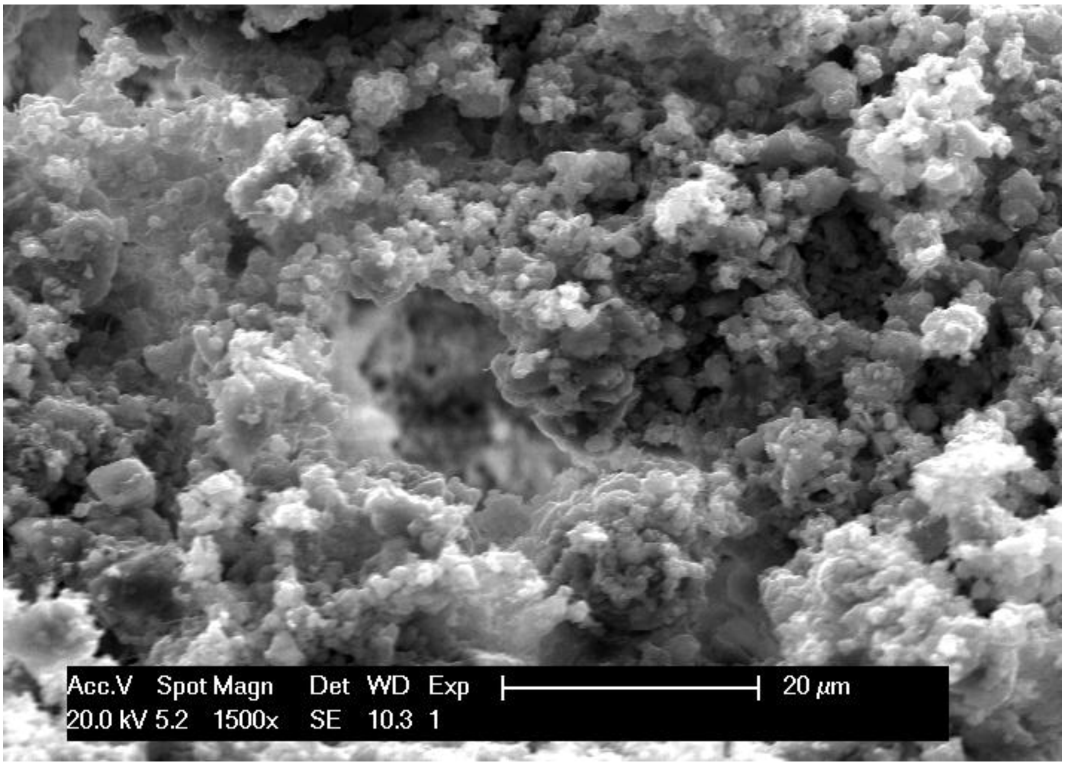


Figure B.14: SEM image of mortar with 10% limestone at 28 days (20-60)

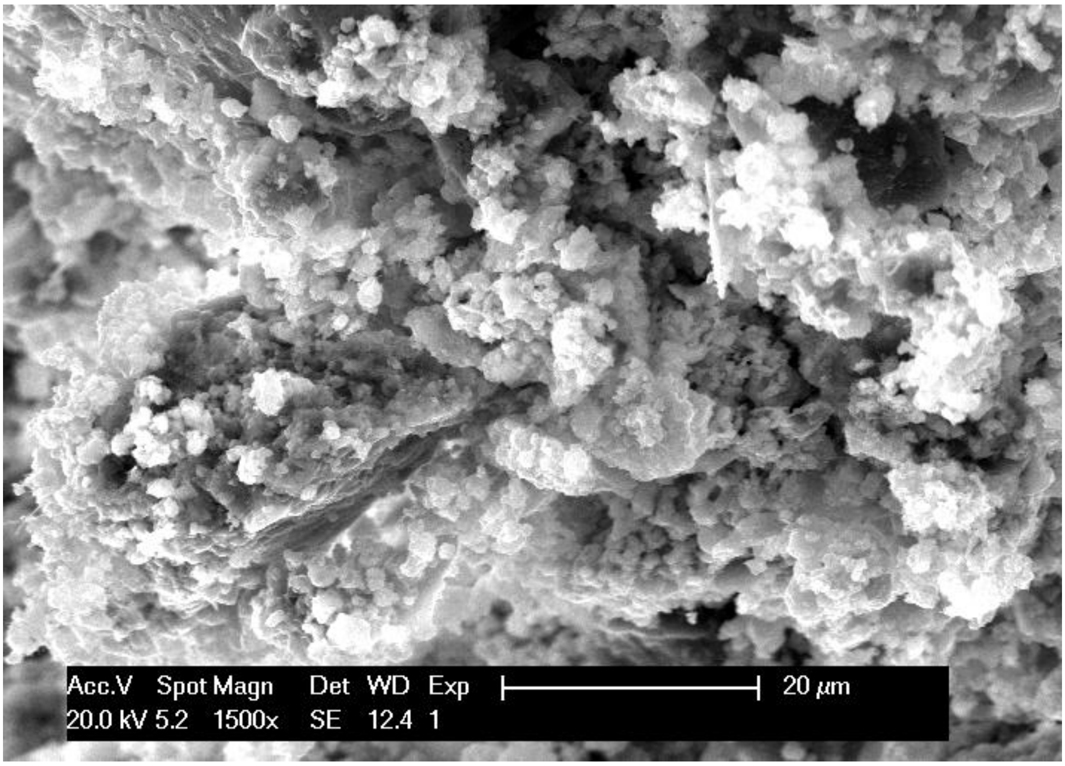


Figure B.15: SEM image of mortar with 10% limestone at 56 days (20-60)

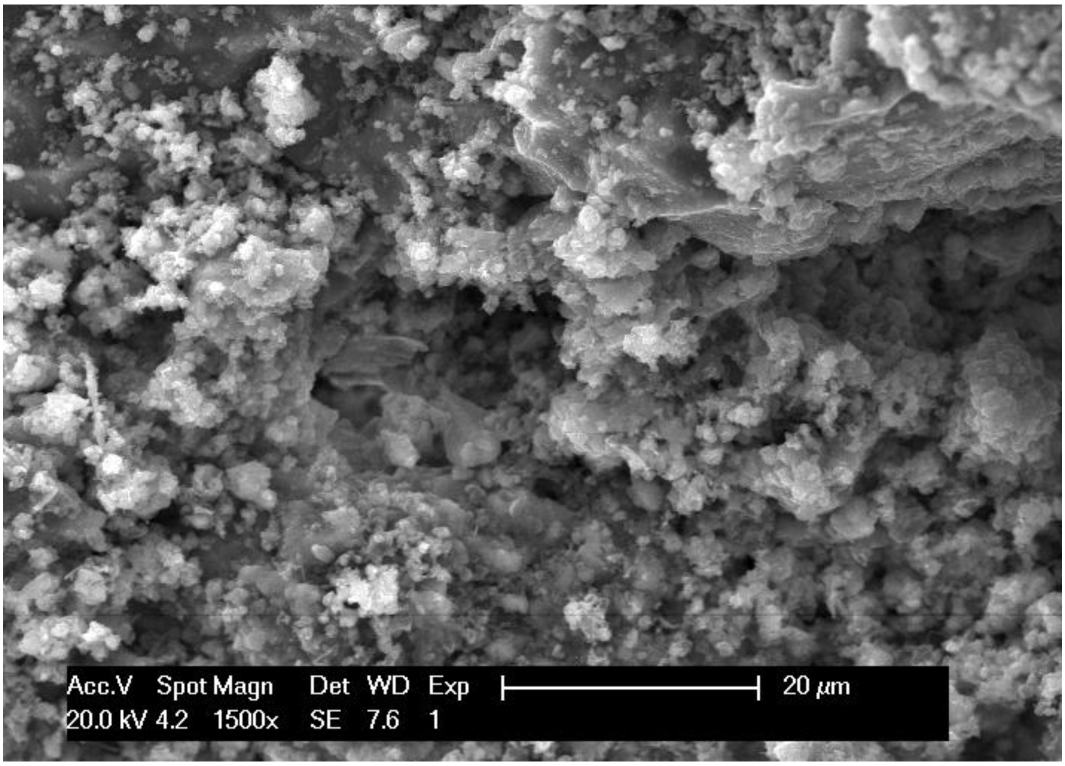


Figure B.16: SEM image of mortar with 6% marble at 7 days (20-60)

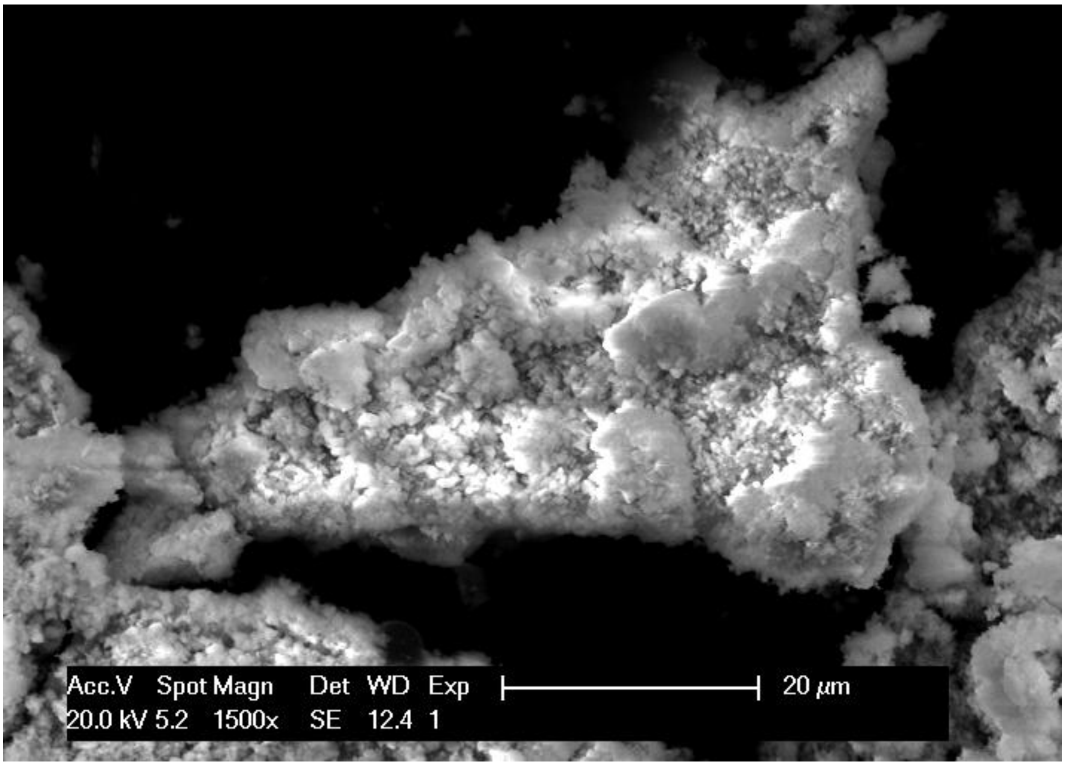


Figure B.17: SEM image of mortar with 6% marble at 28 days (20-60)

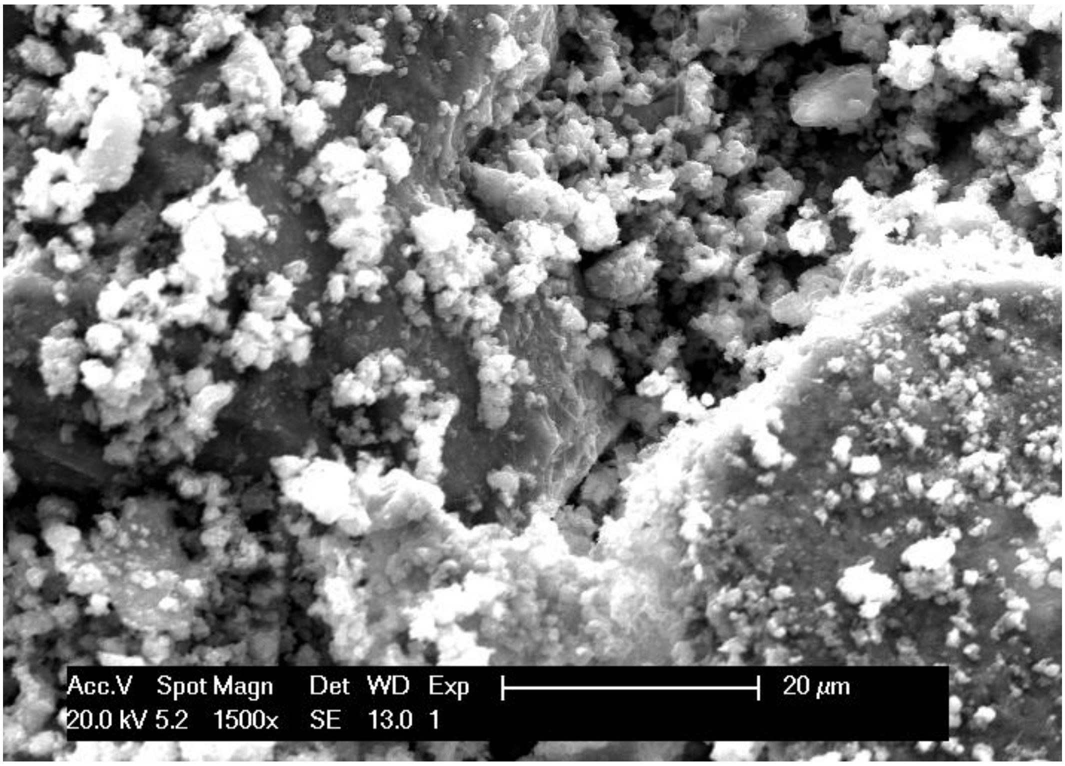


Figure B.18: SEM image of mortar with 6% marble at 56 days (20-60)

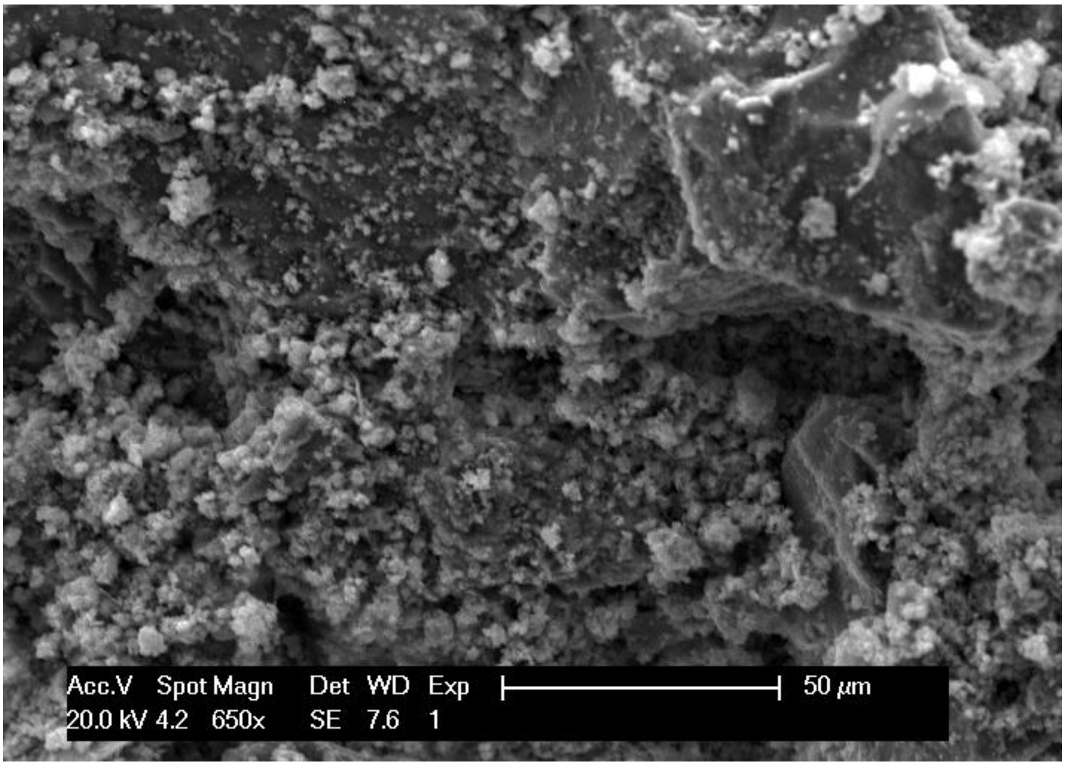


Figure B.19: SEM image of mortar with 10% marble at 7 days (20-60)

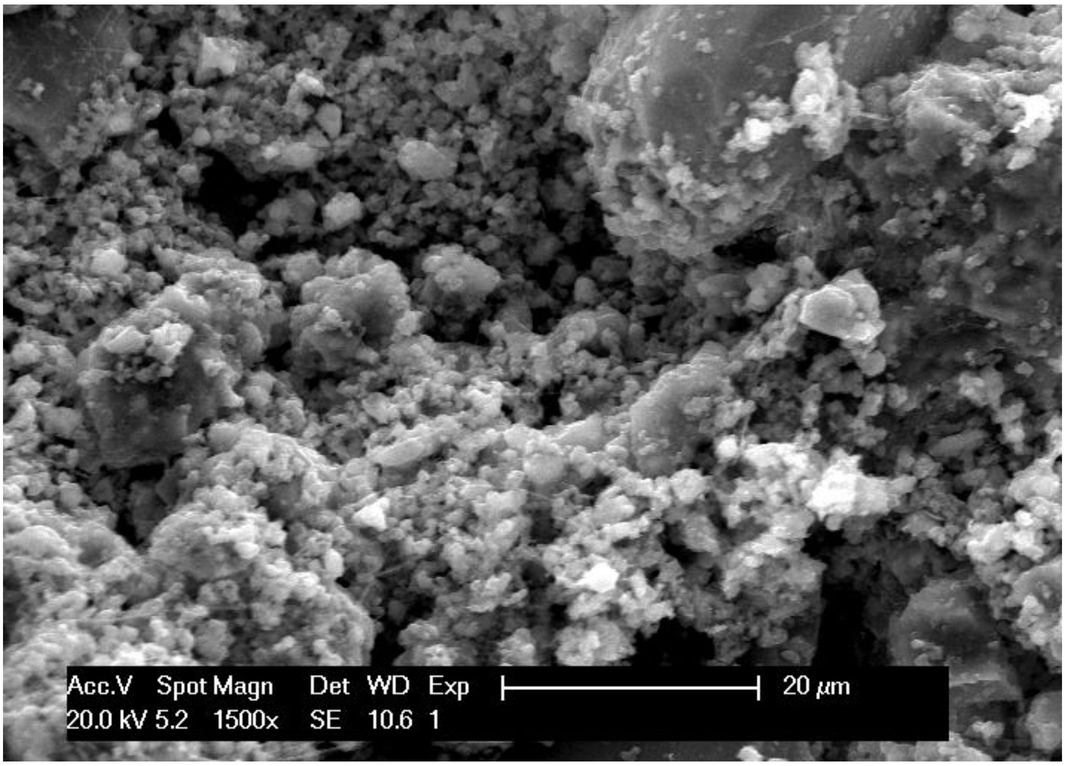


Figure B.20: SEM image of mortar with 10% marble at 28 days (20-60)

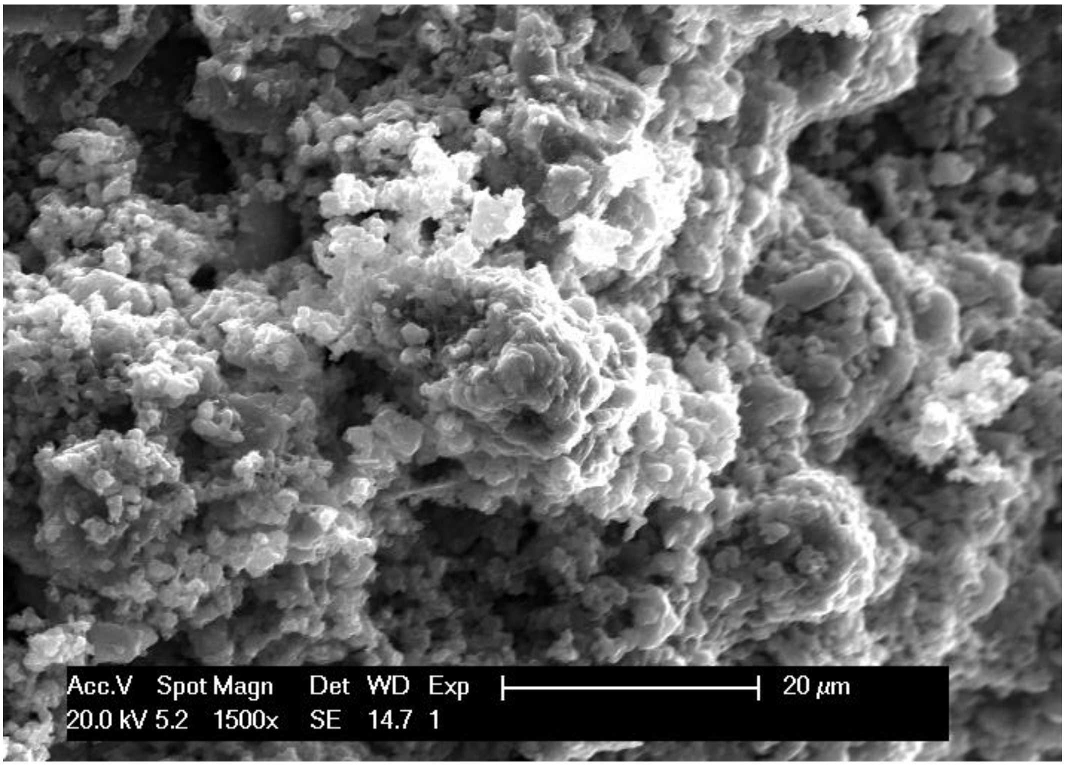


Figure B.21: SEM image of mortar with 10% marble at 56 days (20-60)

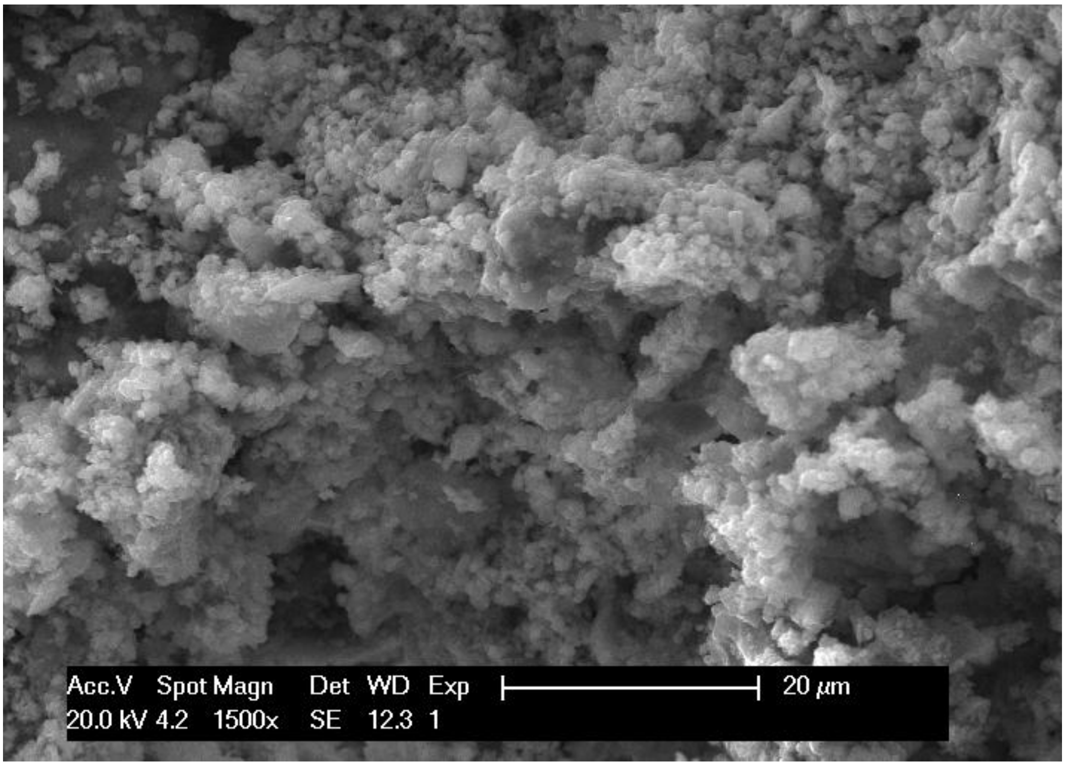


Figure B.22: SEM image of mortar with 6% precipitated $CaCO_3$ at 7 days (20-60)

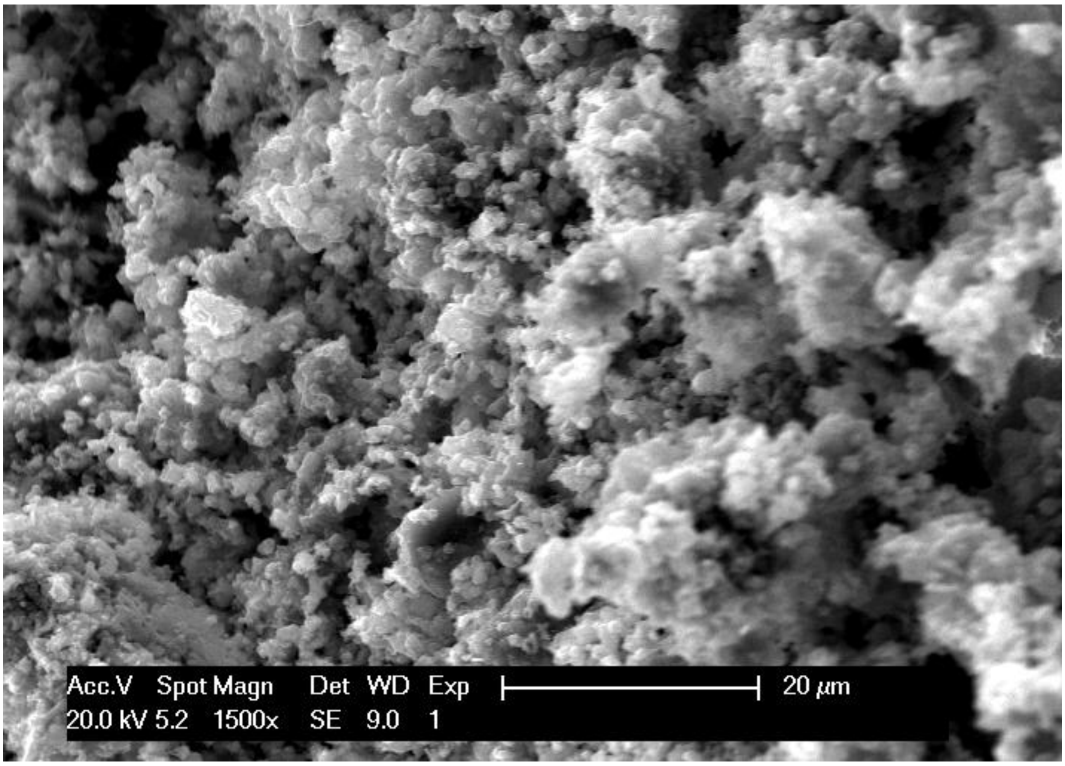


Figure B.23: SEM image of mortar with 6% precipitated $CaCO_3$ at 28 days (20-60)

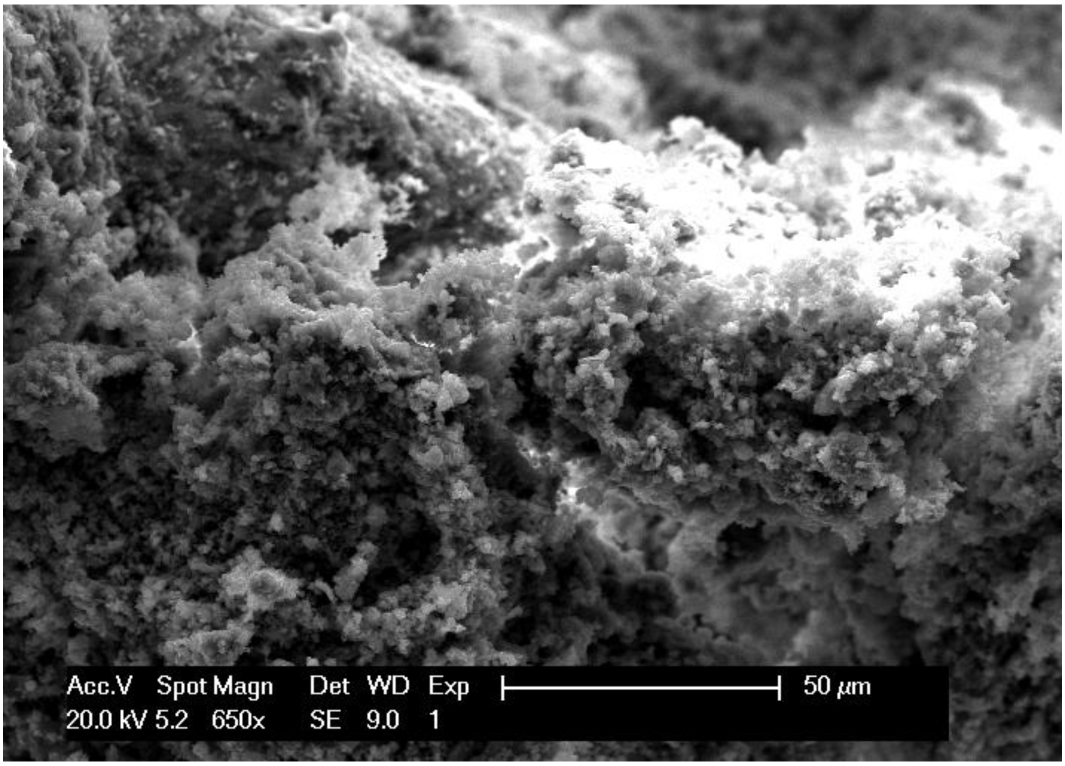


Figure B.24: SEM image of mortar with 6% precipitated $CaCO_3$ at 56 days (20-60)

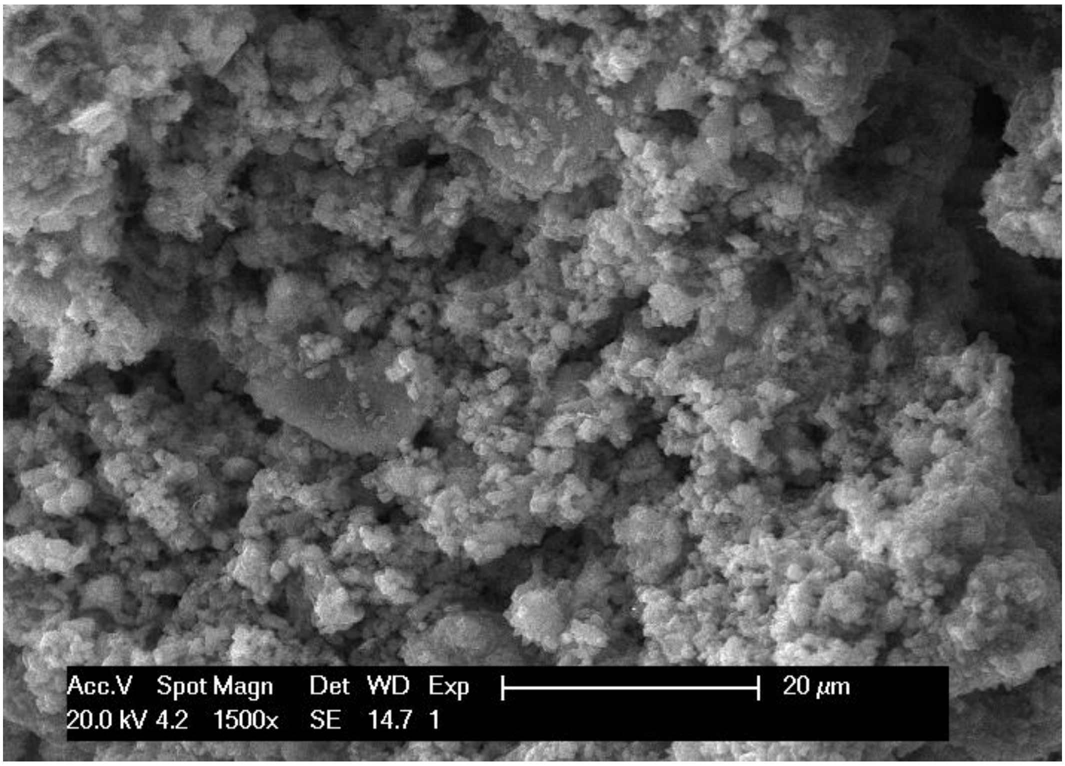


Figure B.25: SEM image of mortar with 10% precipitated $CaCO_3$ at 7 days (20-60)

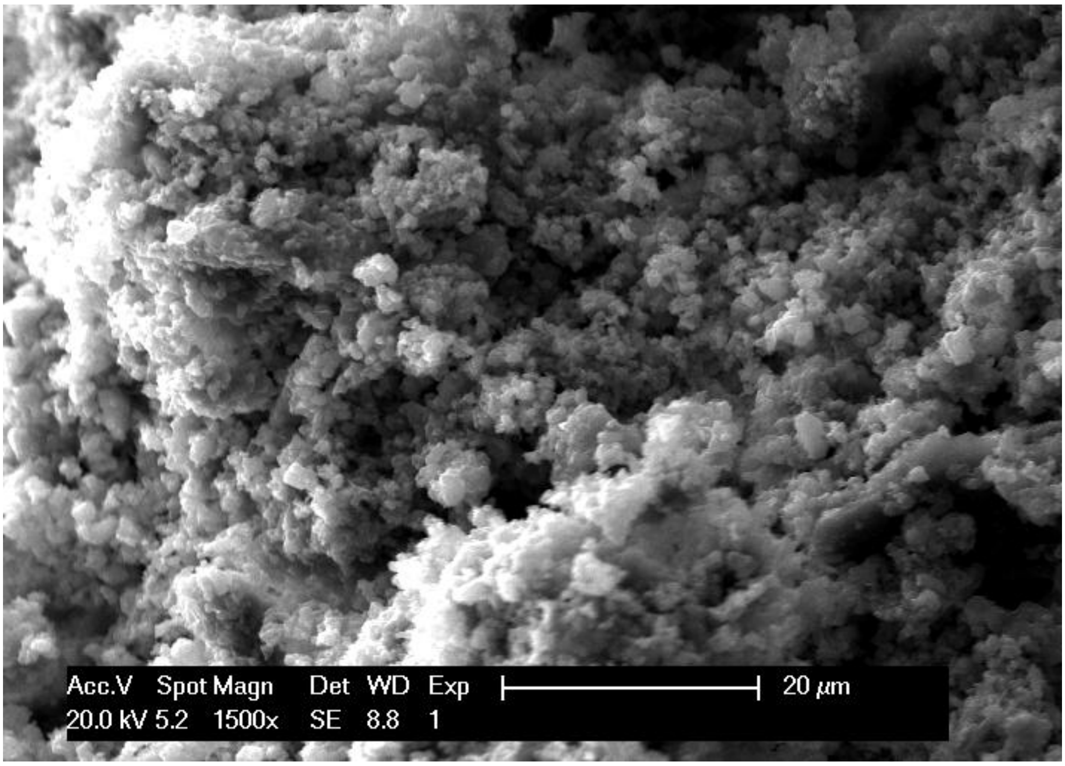


Figure B.26: SEM image of mortar with 10% precipitated $CaCO_3$ at 28 days (20-60)

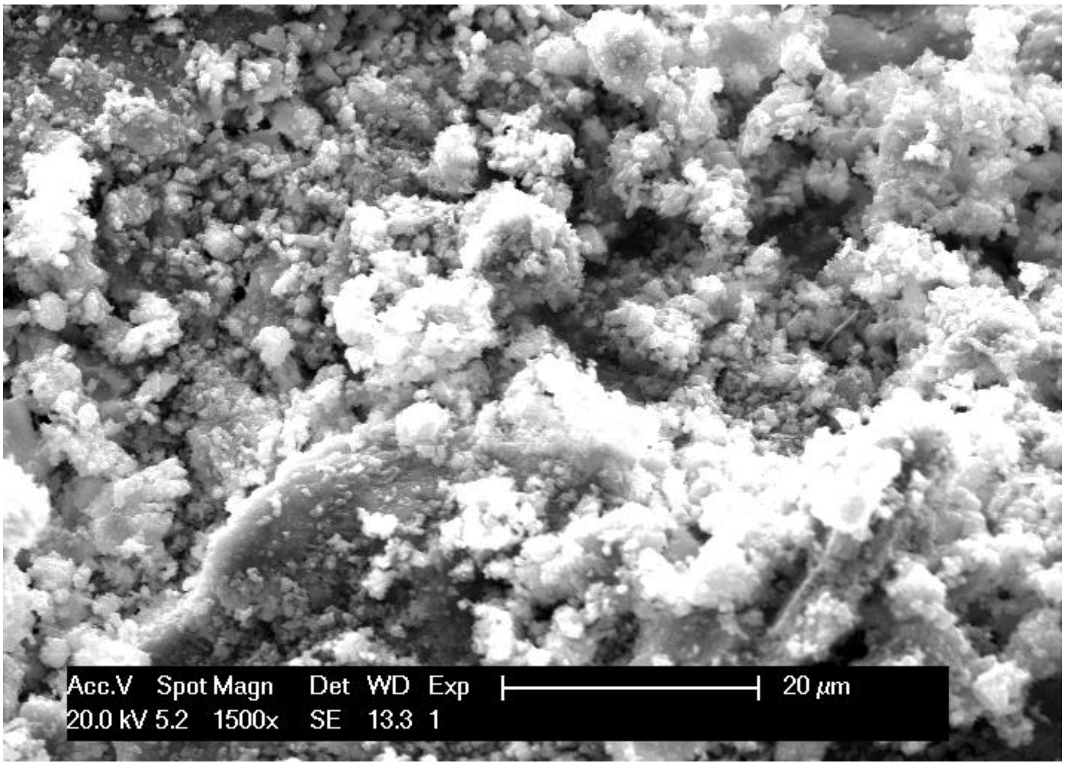


Figure B.27: SEM image of mortar with 10% precipitated $CaCO_3$ at 56 days (20-60)

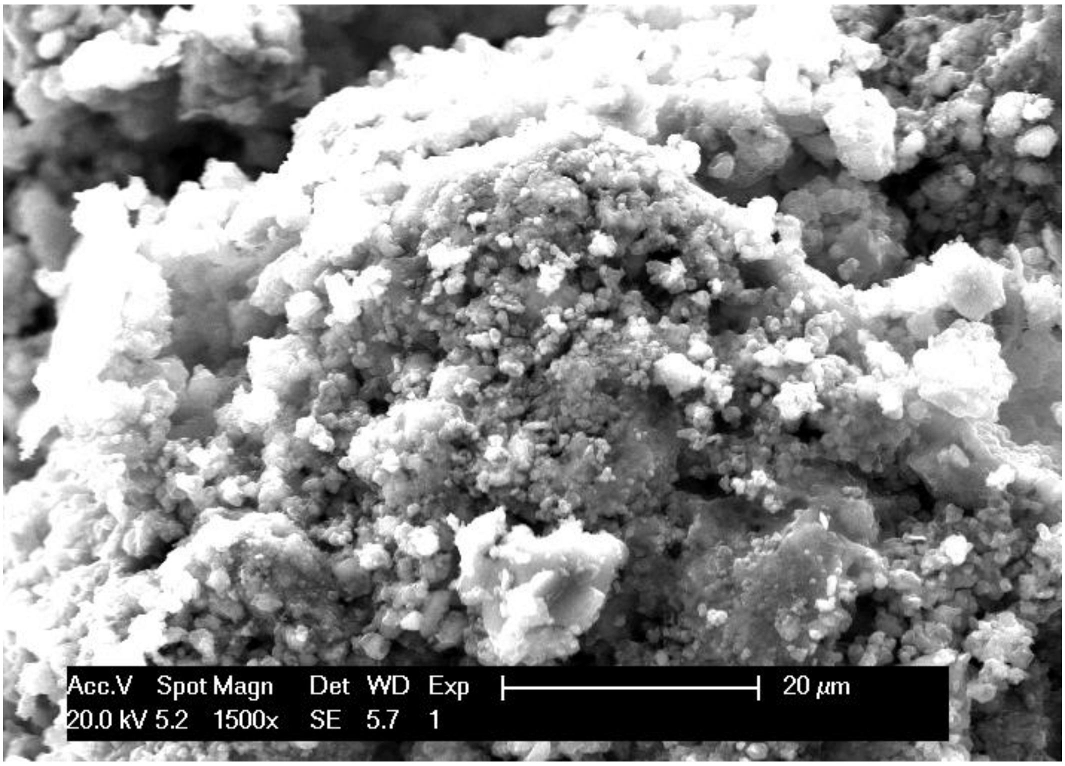


Figure B.28: SEM image of control specimen at 7 days (27-90)

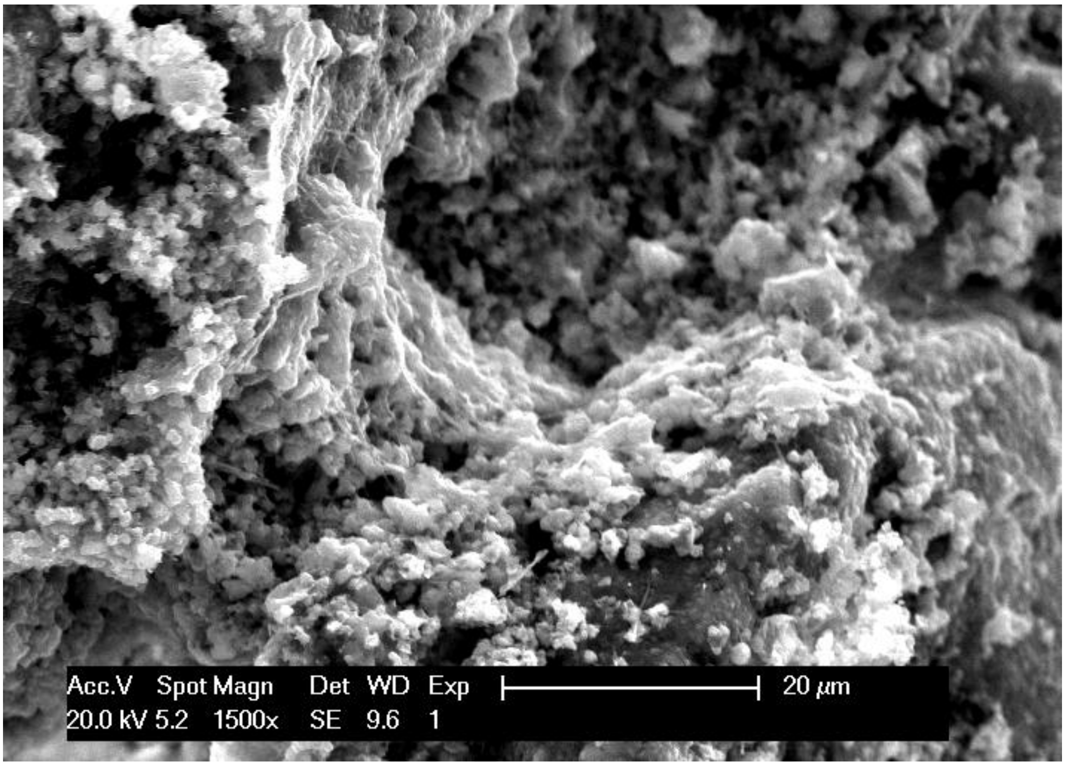


Figure B.29: SEM image of control specimen at 28 days (27-90)

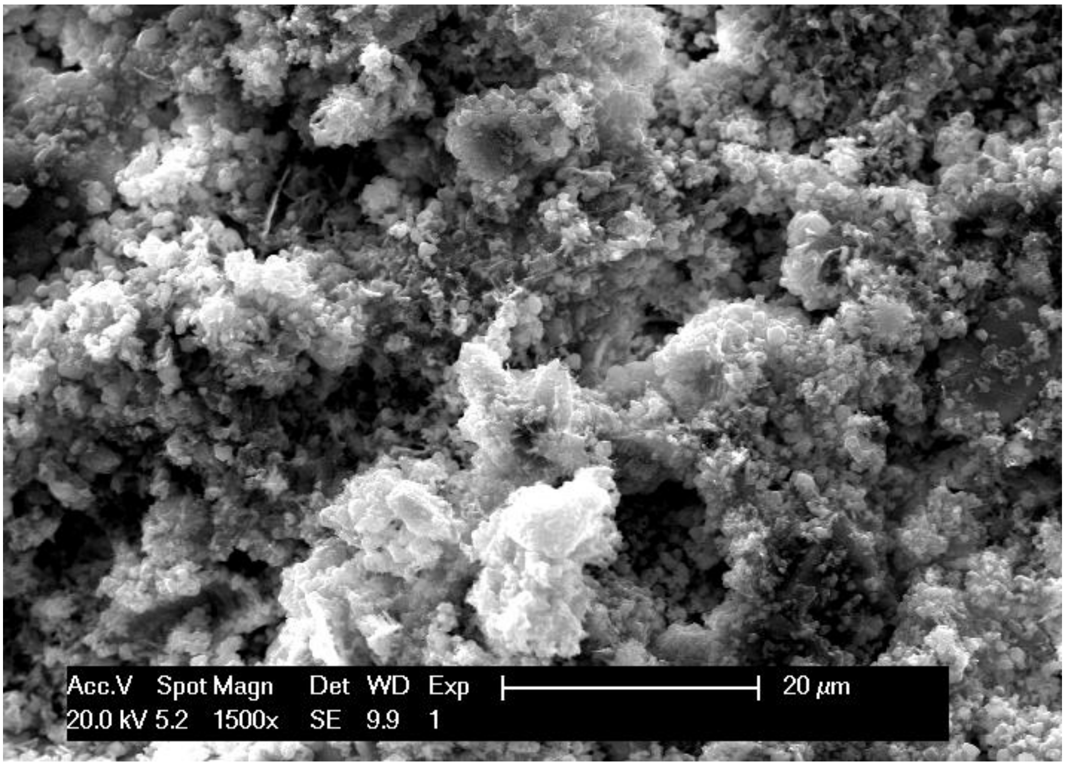


Figure B.30: SEM image of control specimen at 56 days (27-90)

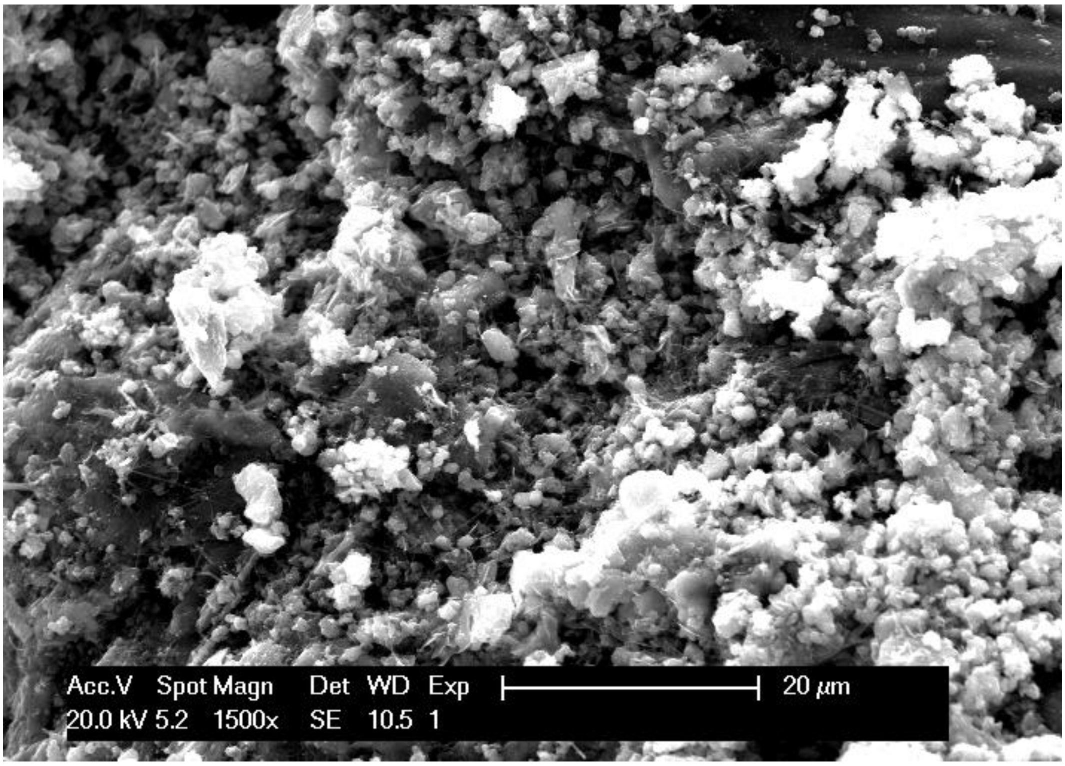


Figure B.31: SEM image of mortar with 6% oyster shells at 7 days (27-90)

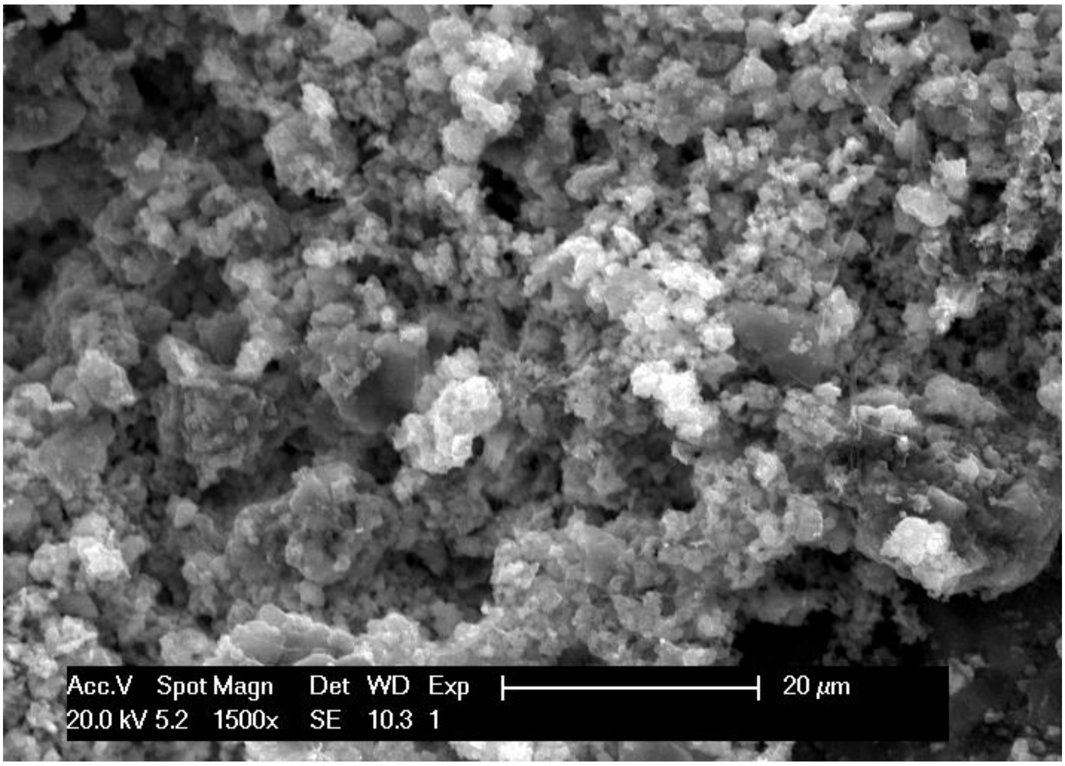


Figure B.32: SEM image of mortar with 6% oyster shells at 28 days (27-90)

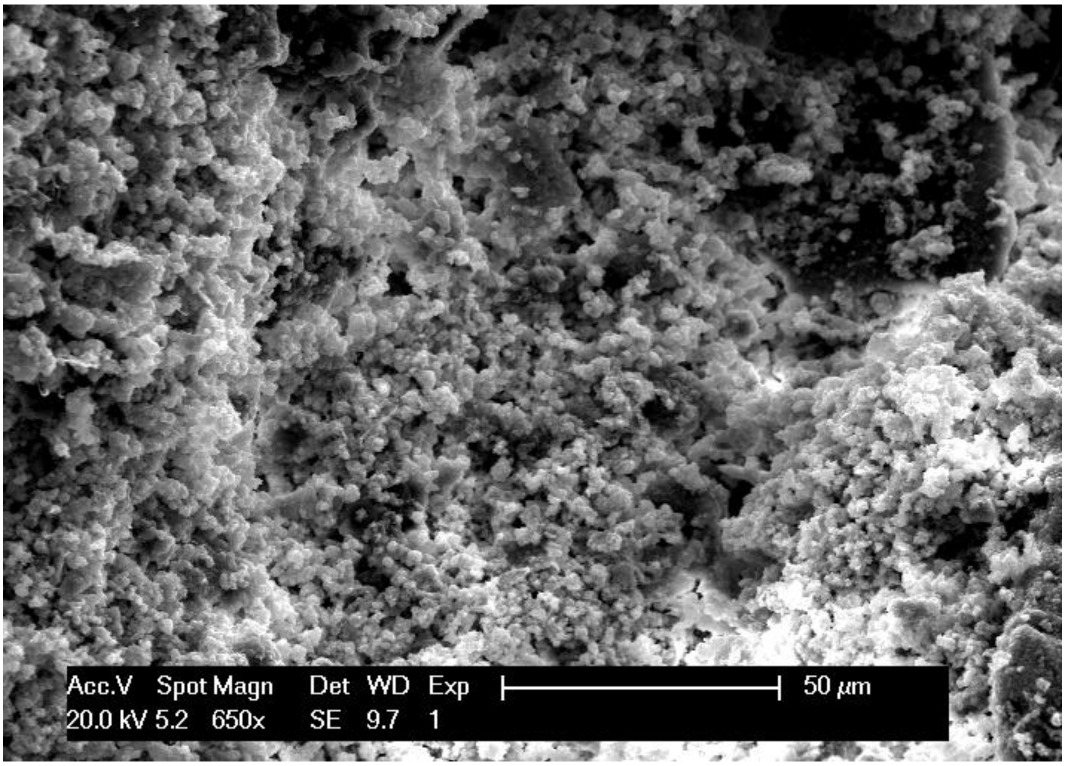


Figure B.33: SEM image of mortar with 6% oyster shells at 56 days (27-90)

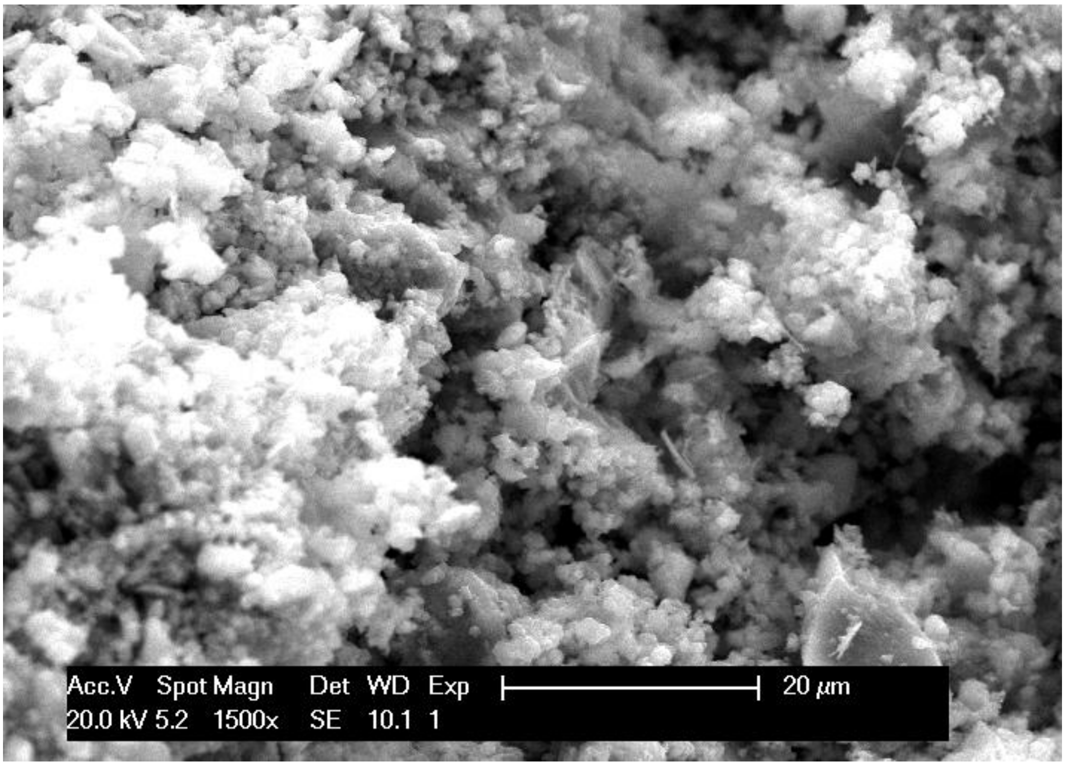


Figure B.34: SEM image of mortar with 10% oyster shells at 7 days (27-90)

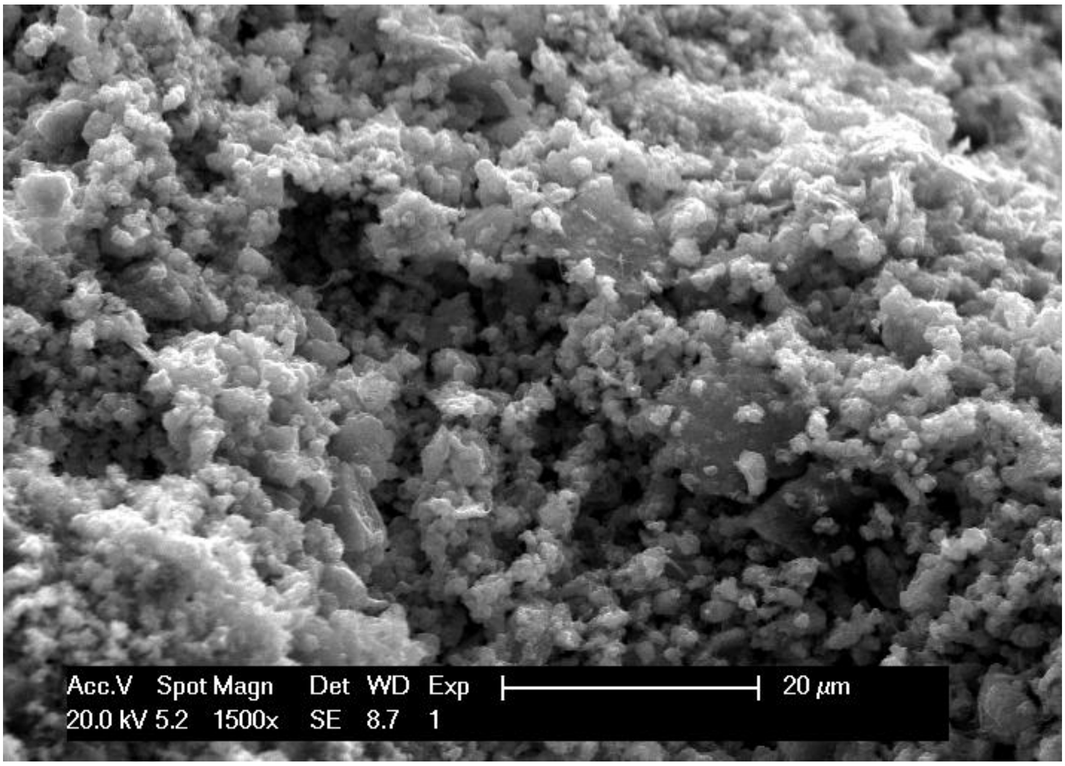


Figure B.35: SEM image of mortar with 10% oyster shells at 28 days (27-90)

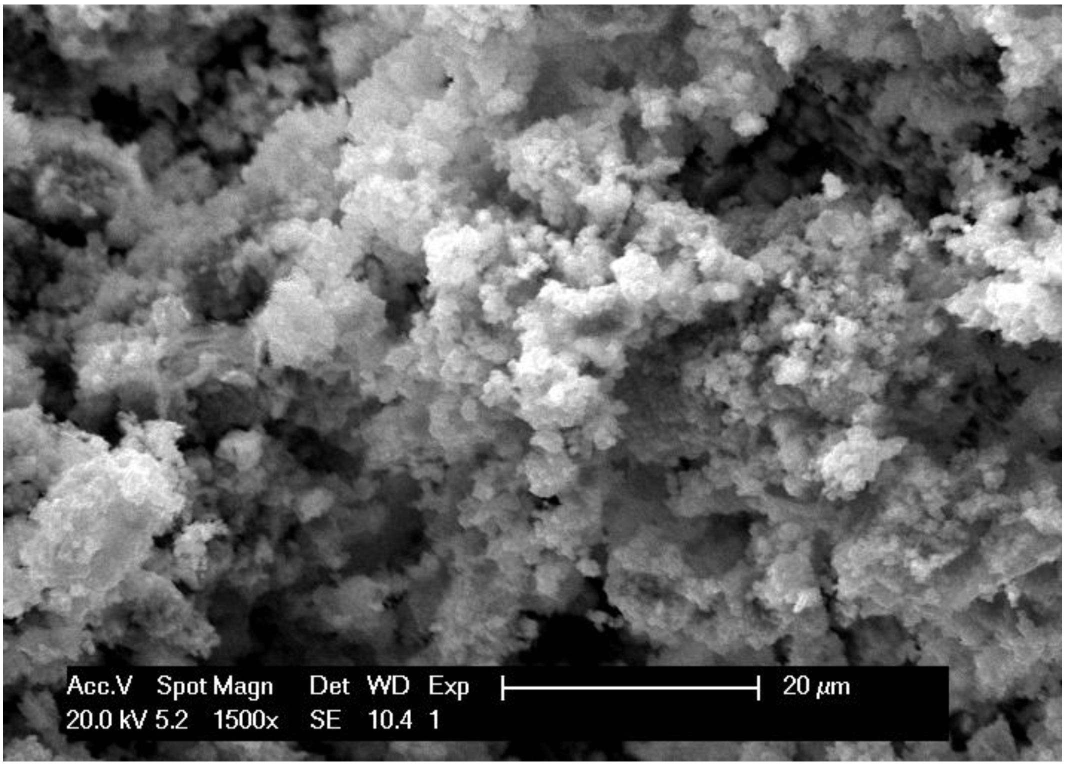


Figure B.36: SEM image of mortar with 10% oyster shells at 56 days (27-90)

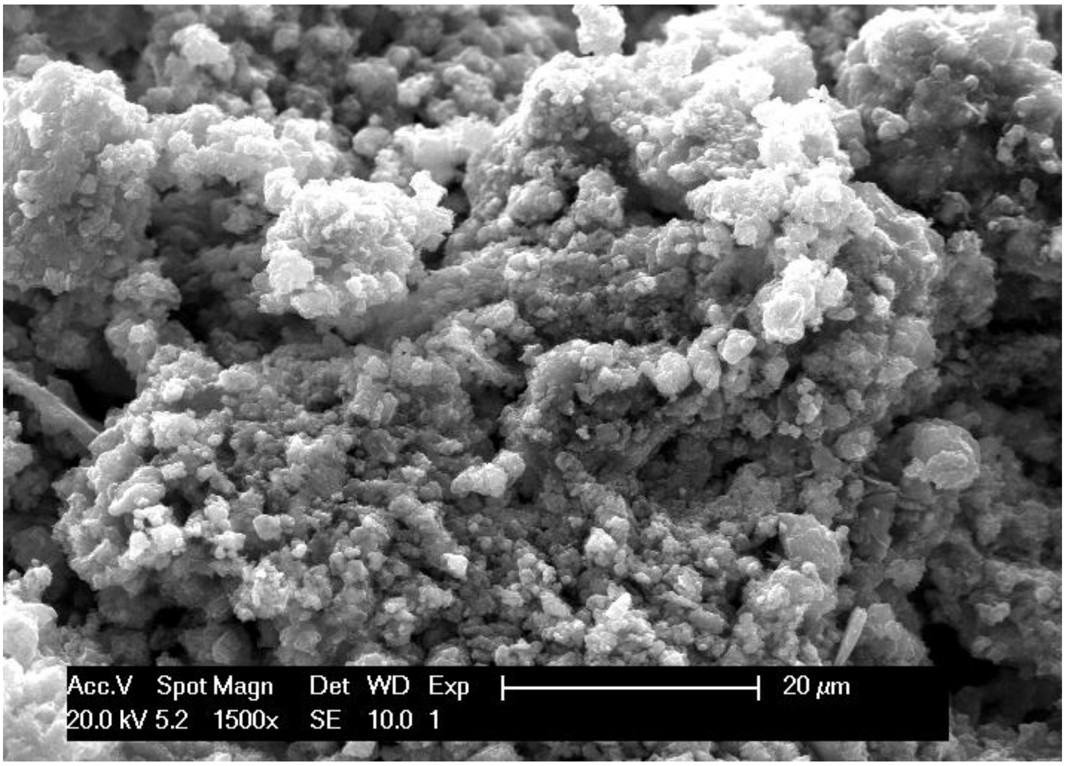


Figure B.37: SEM image of mortar with 6% limestone at 7 days (27-90)

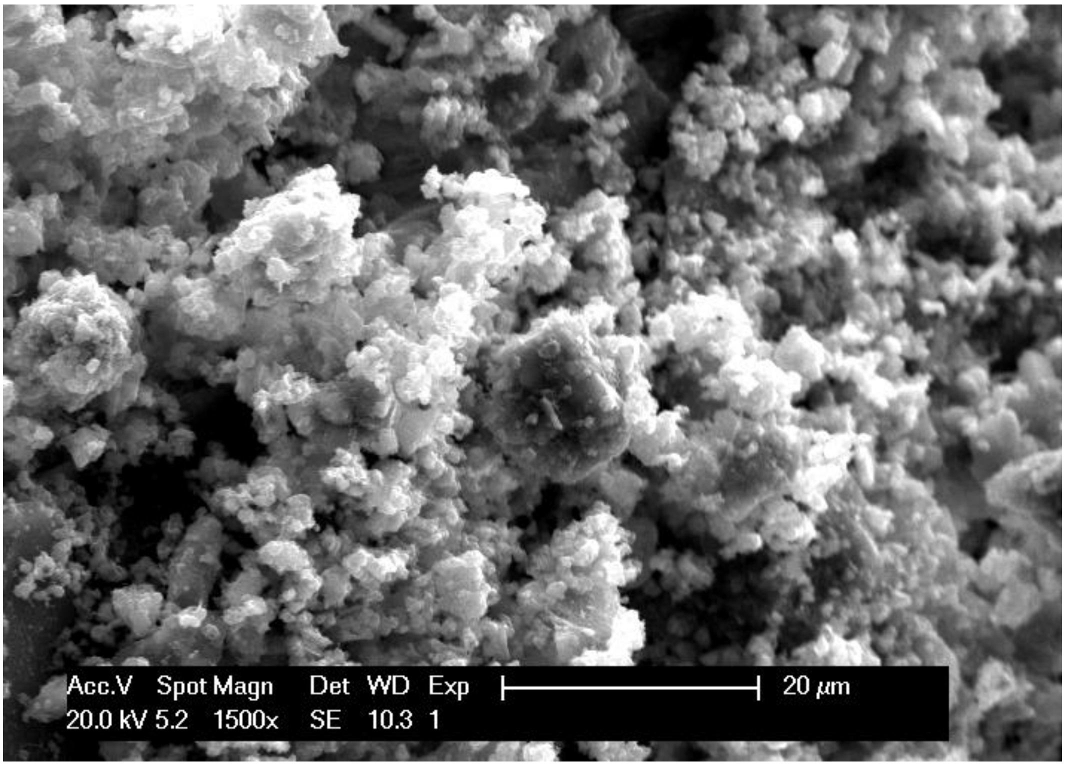


Figure B.38: SEM image of mortar with 6% limestone at 28 days (27-90)

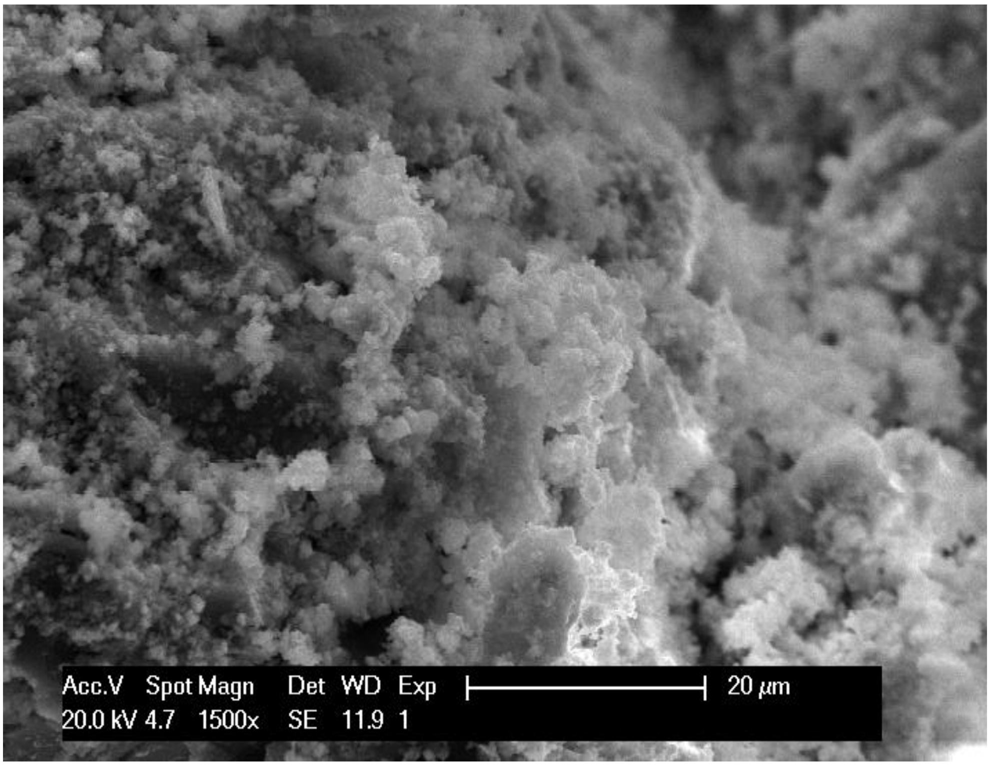


Figure B.39: SEM image of mortar with 6% limestone at 56 days (27-90)

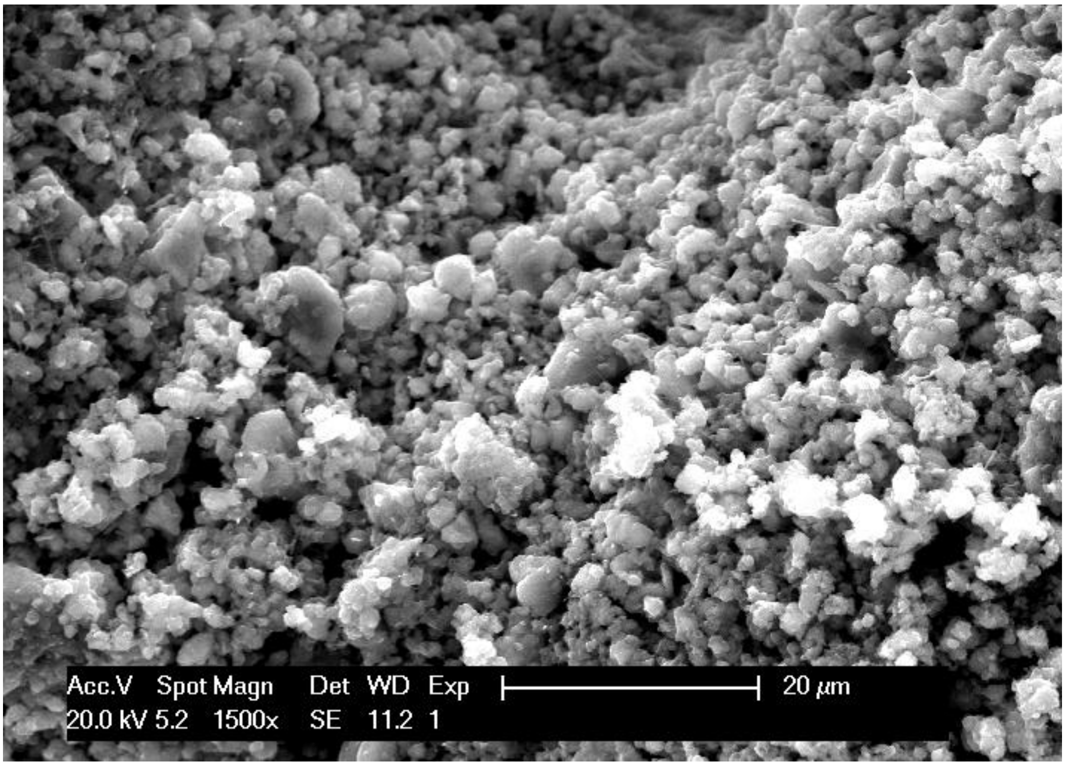


Figure B.40: SEM image of mortar with 10% limestone at 7 days (27-90)

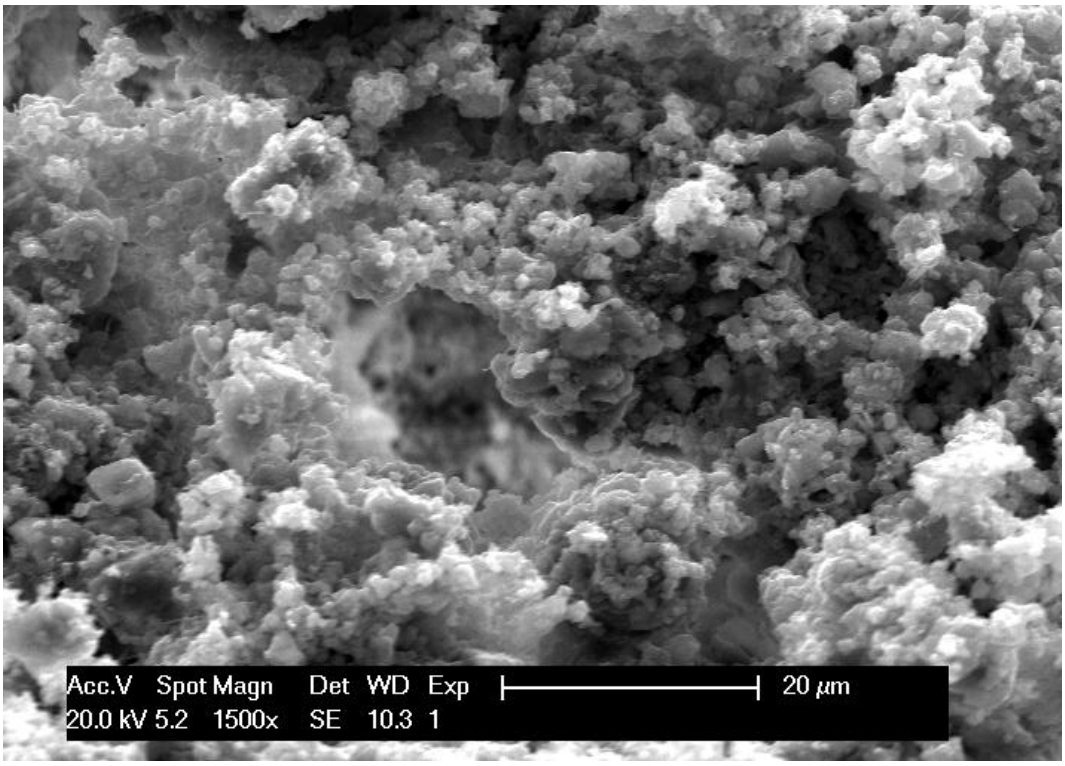


Figure B.41: SEM image of mortar with 10% limestone at 28 days (27-90)

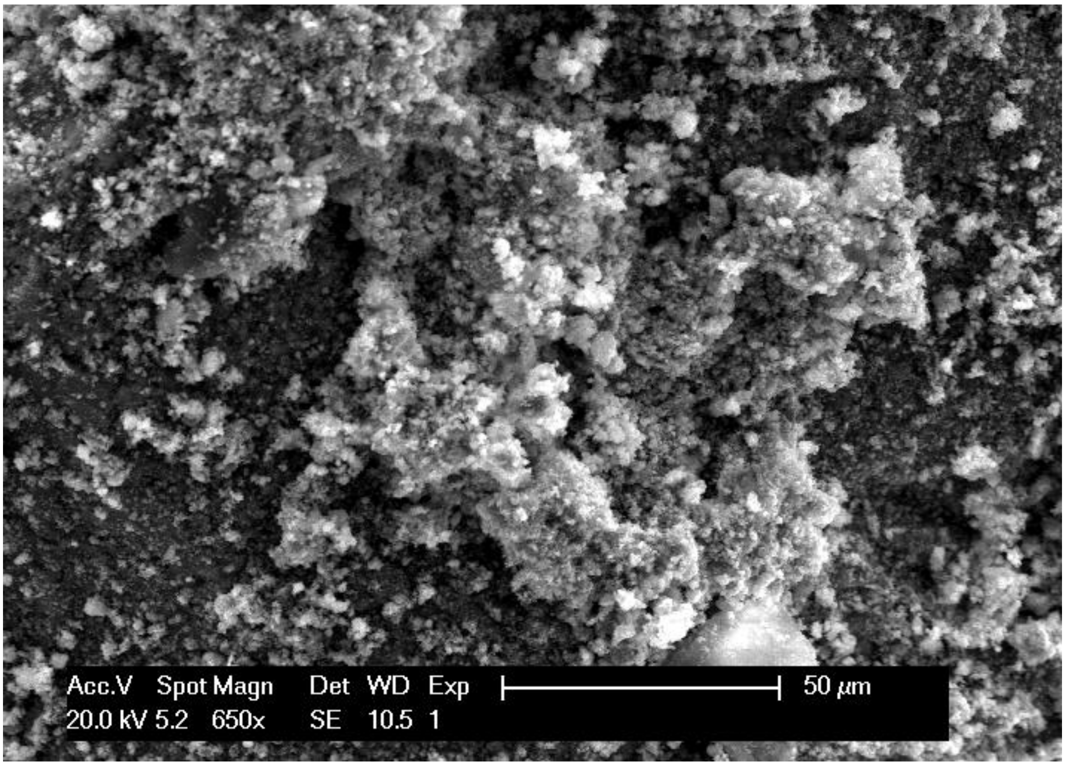


Figure B.42: SEM image of mortar with 10% limestone at 56 days (27-90)

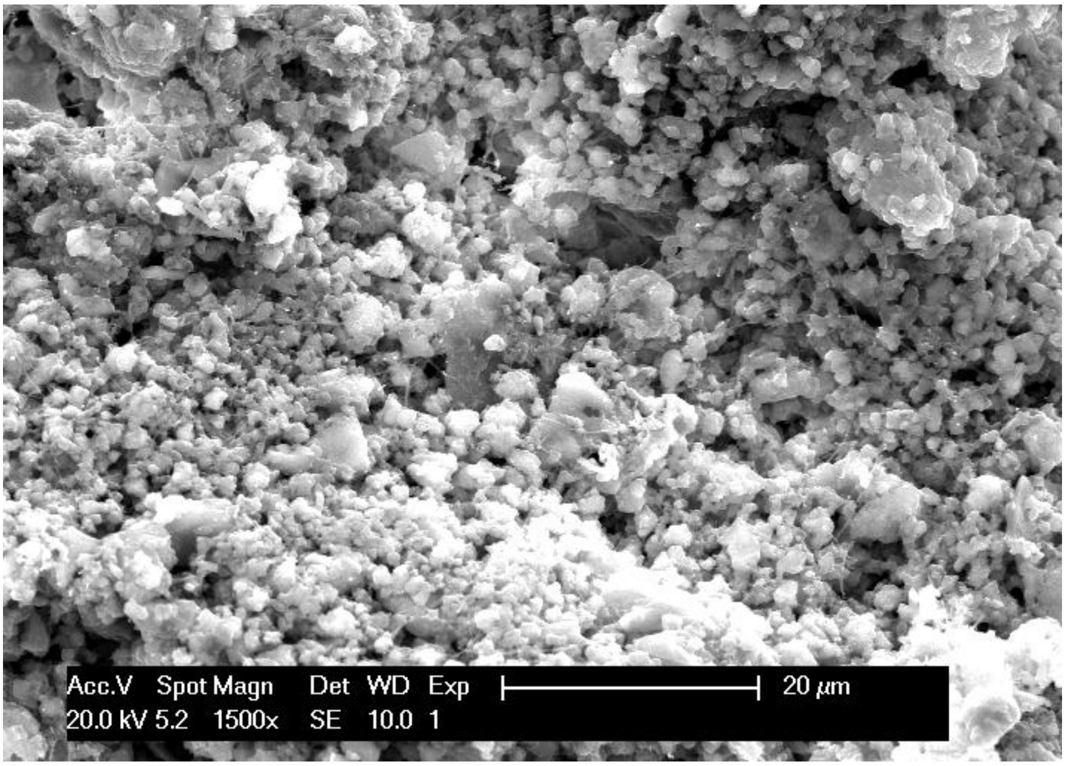


Figure B.43: SEM image of mortar with 6% marble at 7 days (27-90)

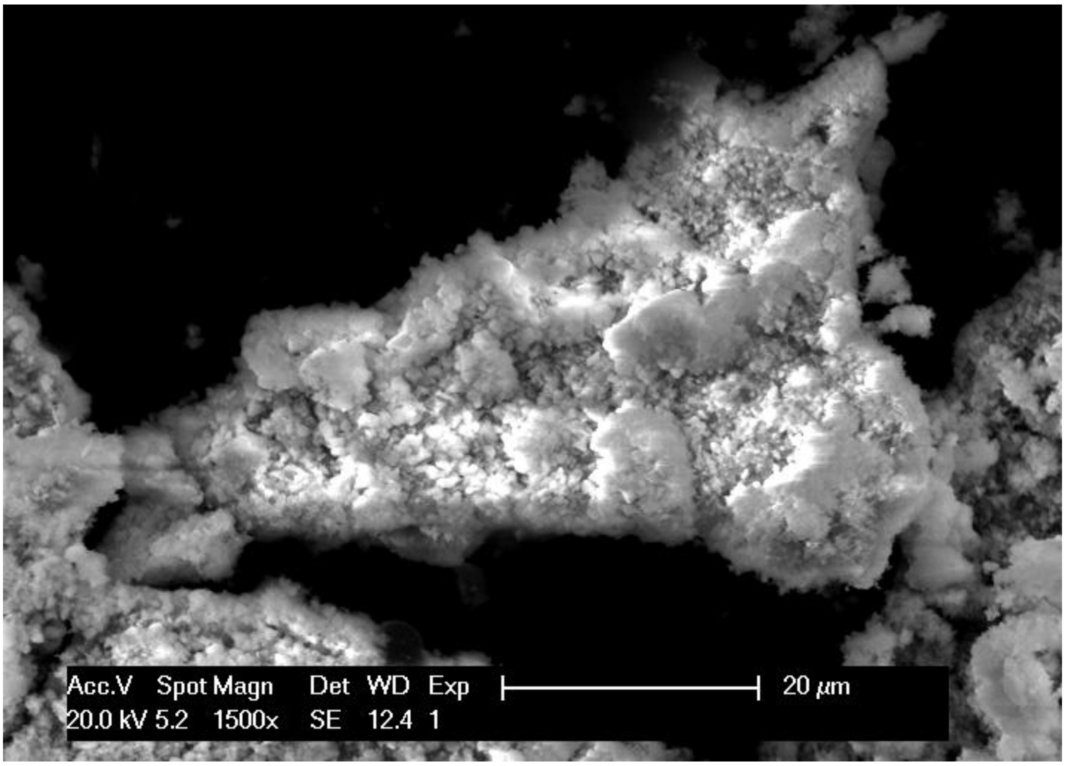


Figure B.44: SEM image of mortar with 6% marble at 28 days (27-90)

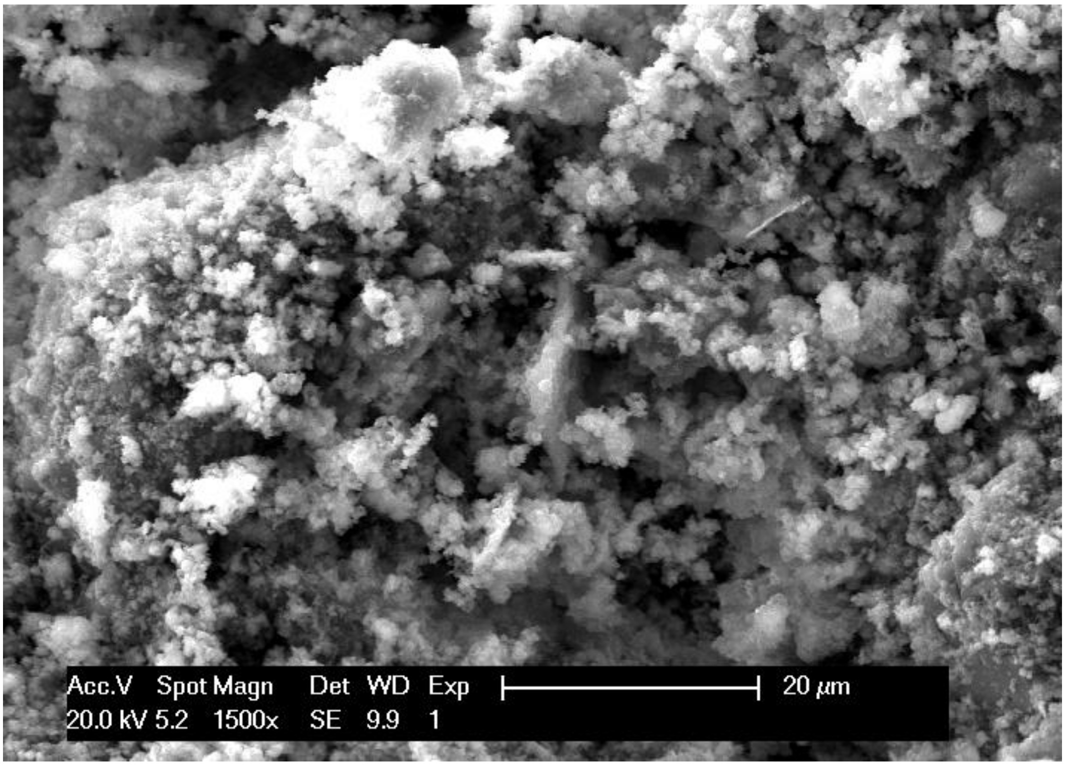


Figure B.45: SEM image of mortar with 6% marble at 56 days (27-90)

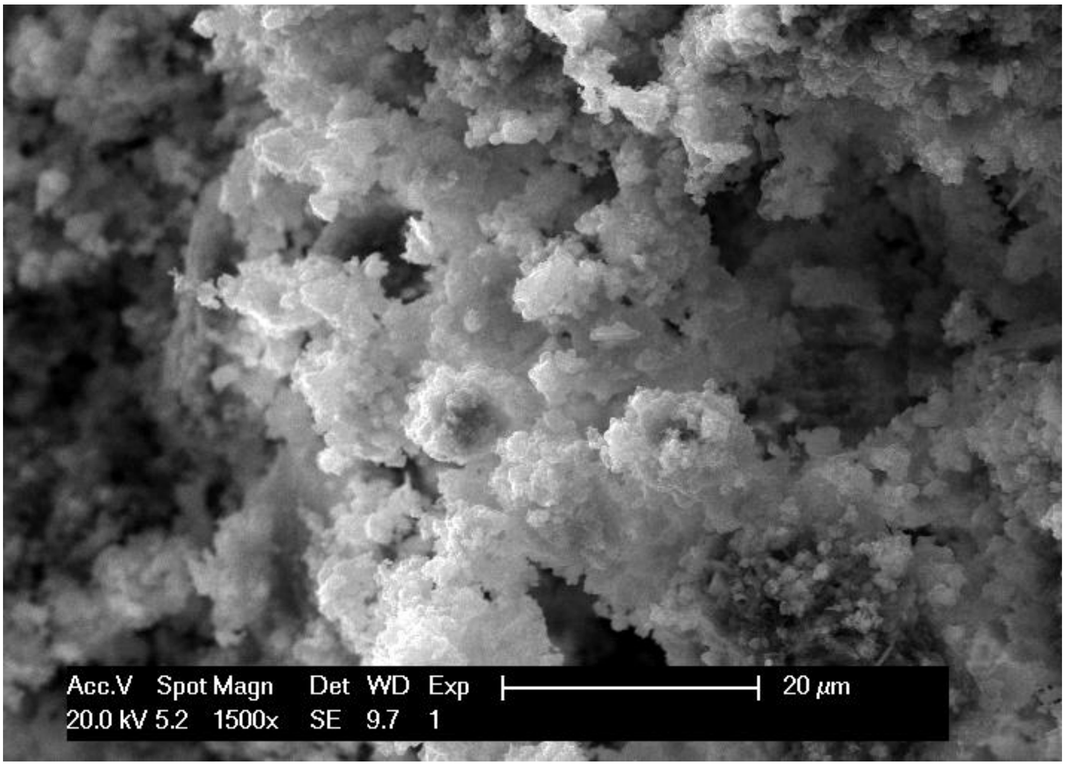


Figure B.46: SEM image of mortar with 10% marble at 7 days (27-90)

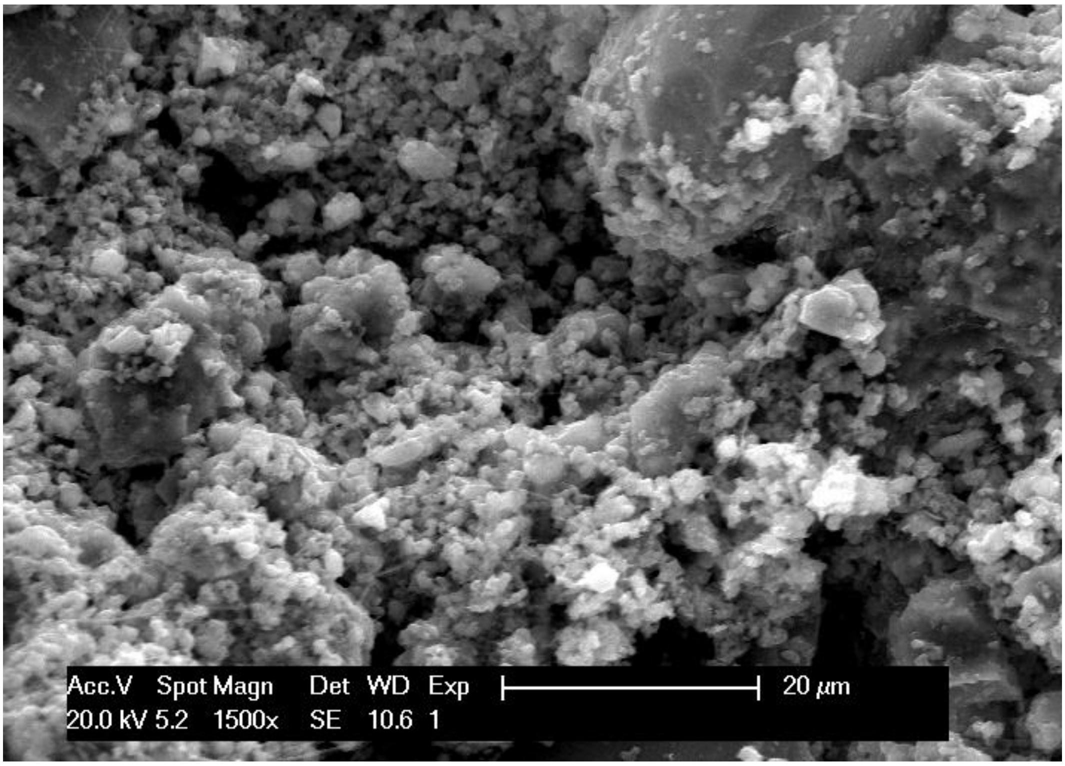


Figure B.47: SEM image of mortar with 10% marble at 28 days (27-90)

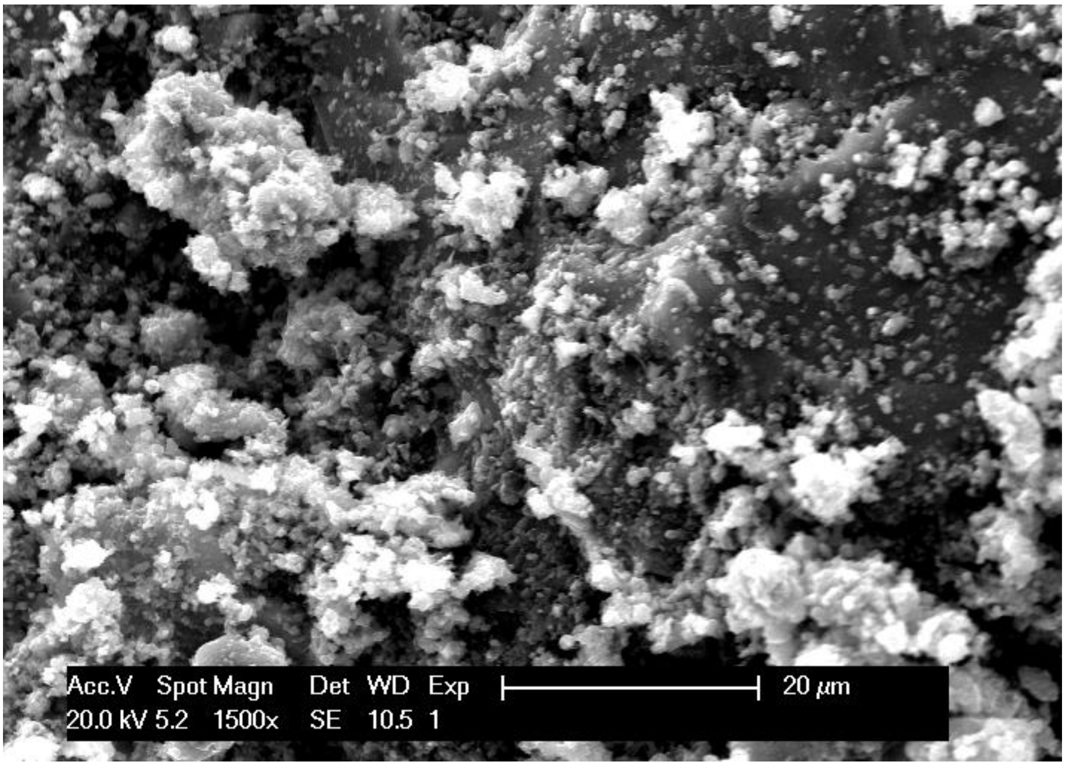


Figure B.48: SEM image of mortar with 10% marble at 56 days (27-90)

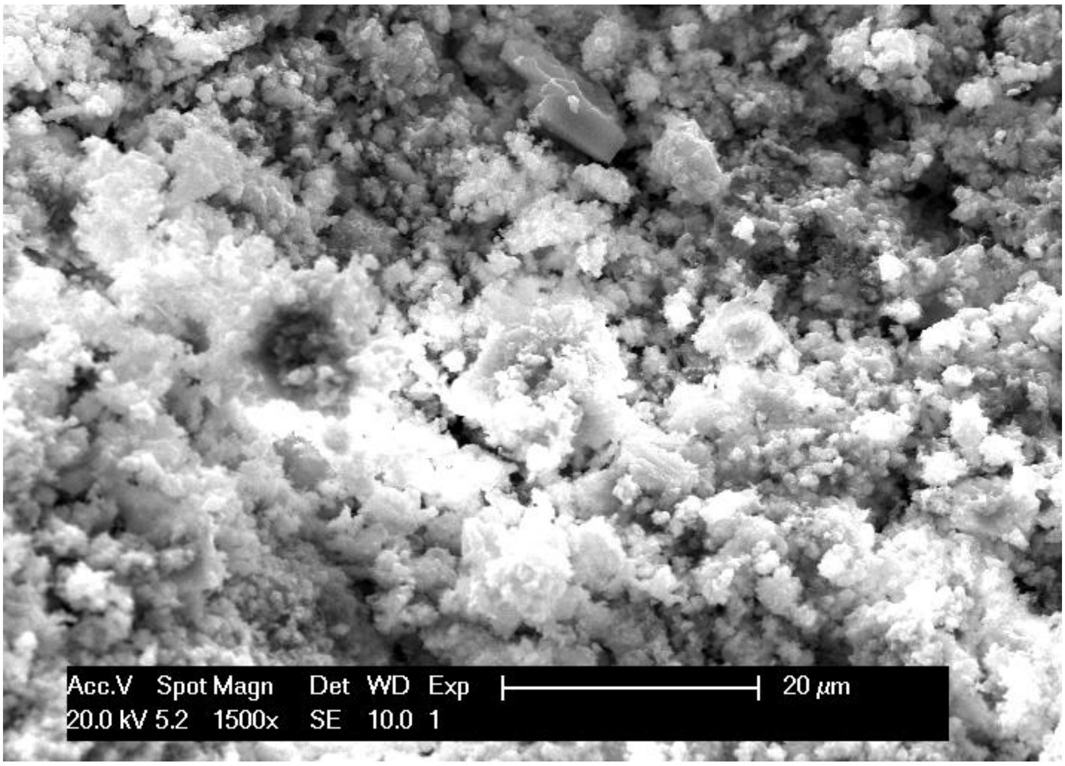


Figure B.49: SEM image of mortar with 6% precipitated $CaCO_3$ at 7 days (27-90)

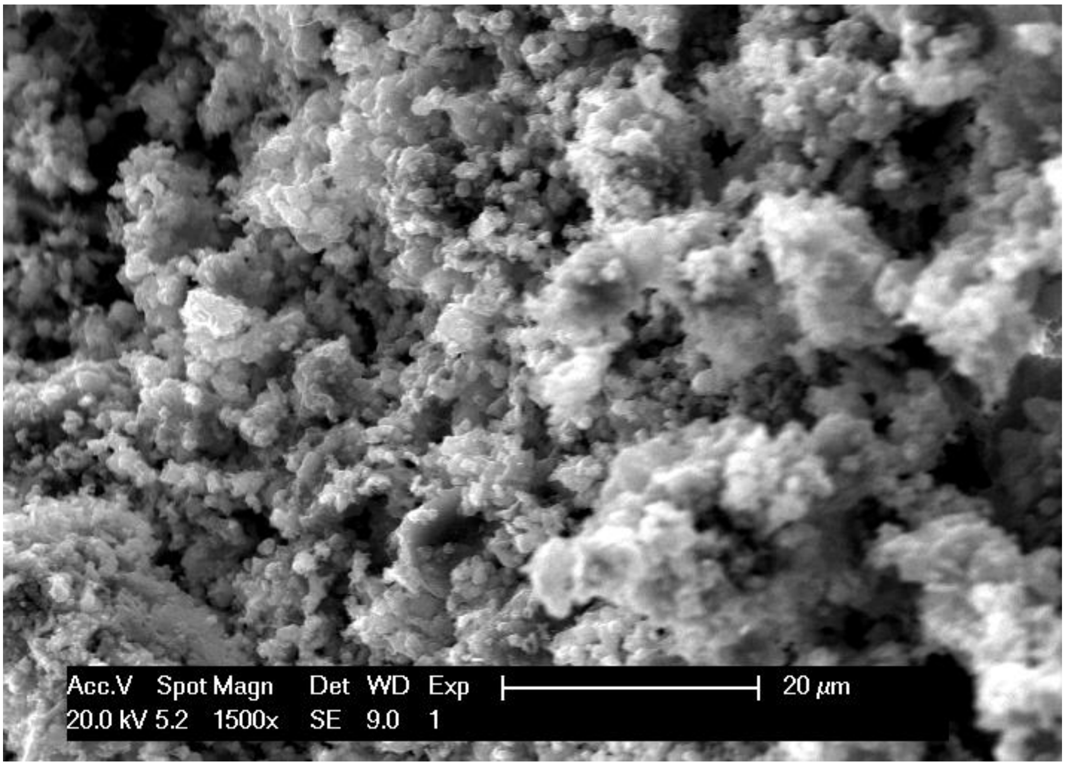


Figure B.50: SEM image of mortar with 6% precipitated $CaCO_3$ at 28 days (27-90)

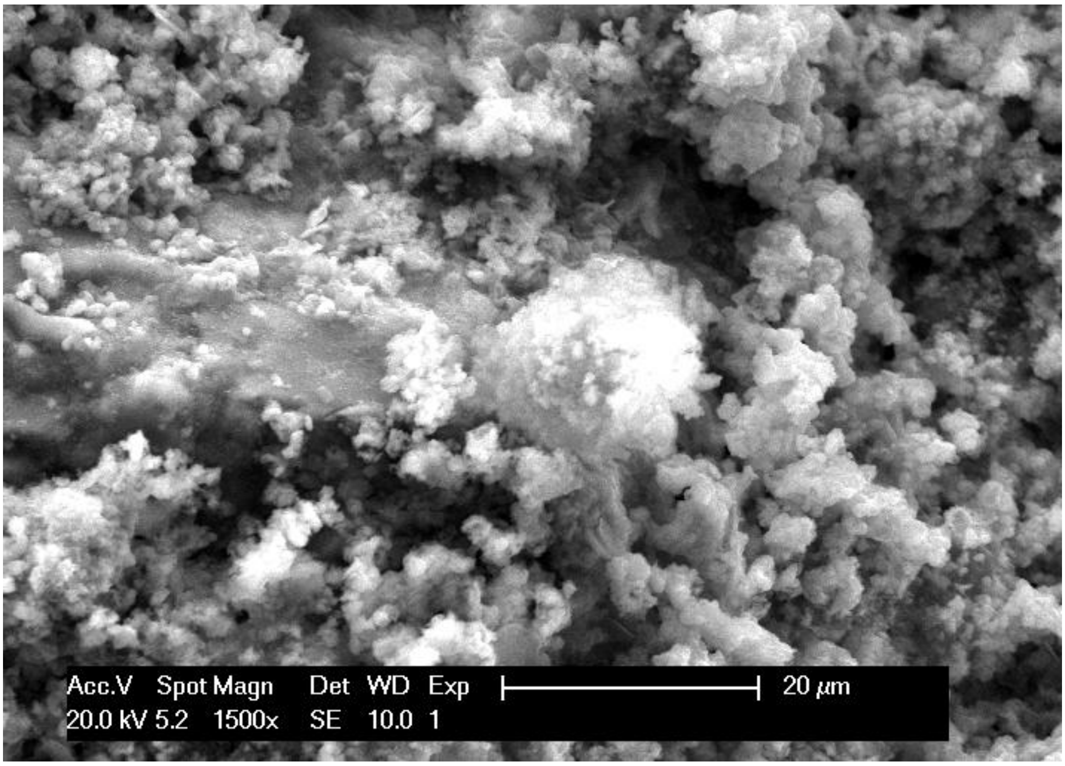


Figure B.51: SEM image of mortar with 6% precipitated $CaCO_3$ at 56 days (27-90)

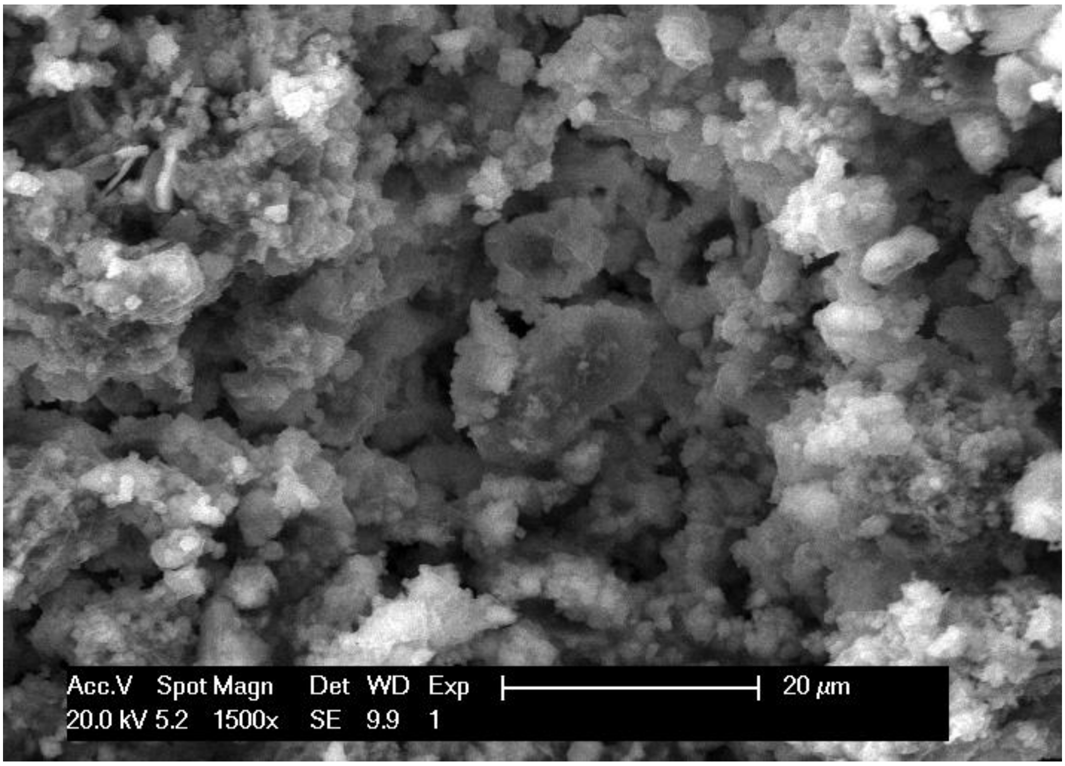


Figure B.52: SEM image of mortar with 10% precipitated $CaCO_3$ at 7 days (27-90)

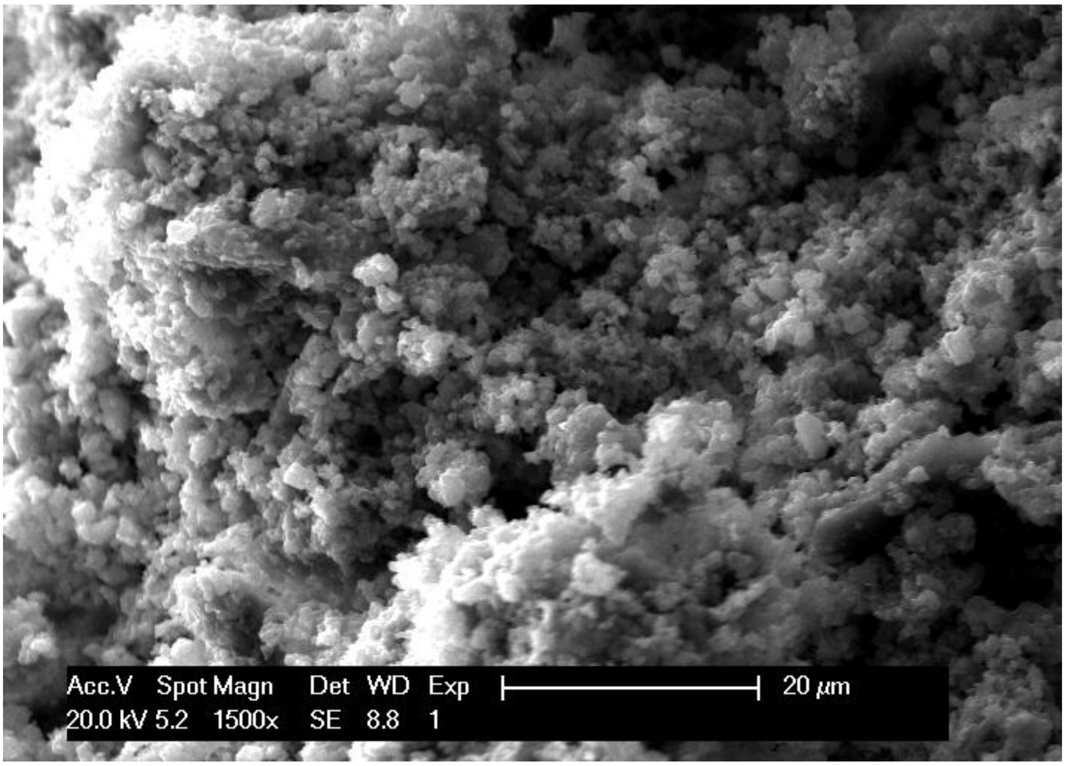


Figure B.53: SEM image of mortar with 10% precipitated $CaCO_3$ at 28 days (27-90)

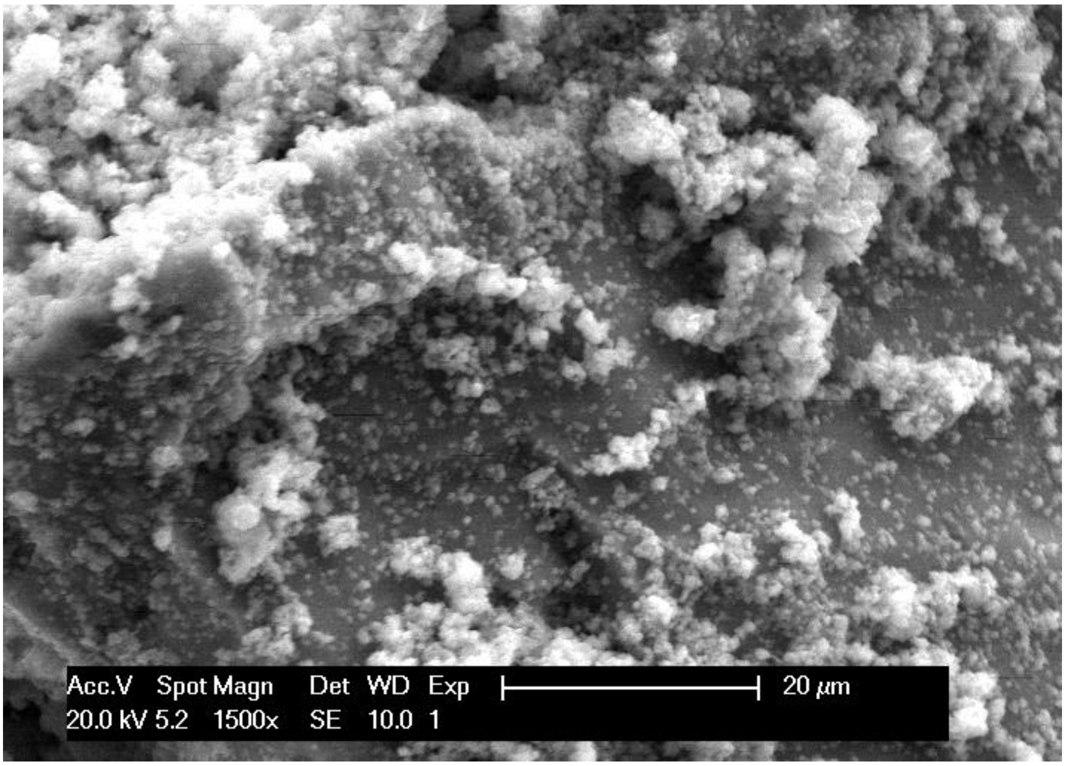


Figure B.54: SEM image of mortar with 10% precipitated $CaCO_3$ at 56 days (27-90)

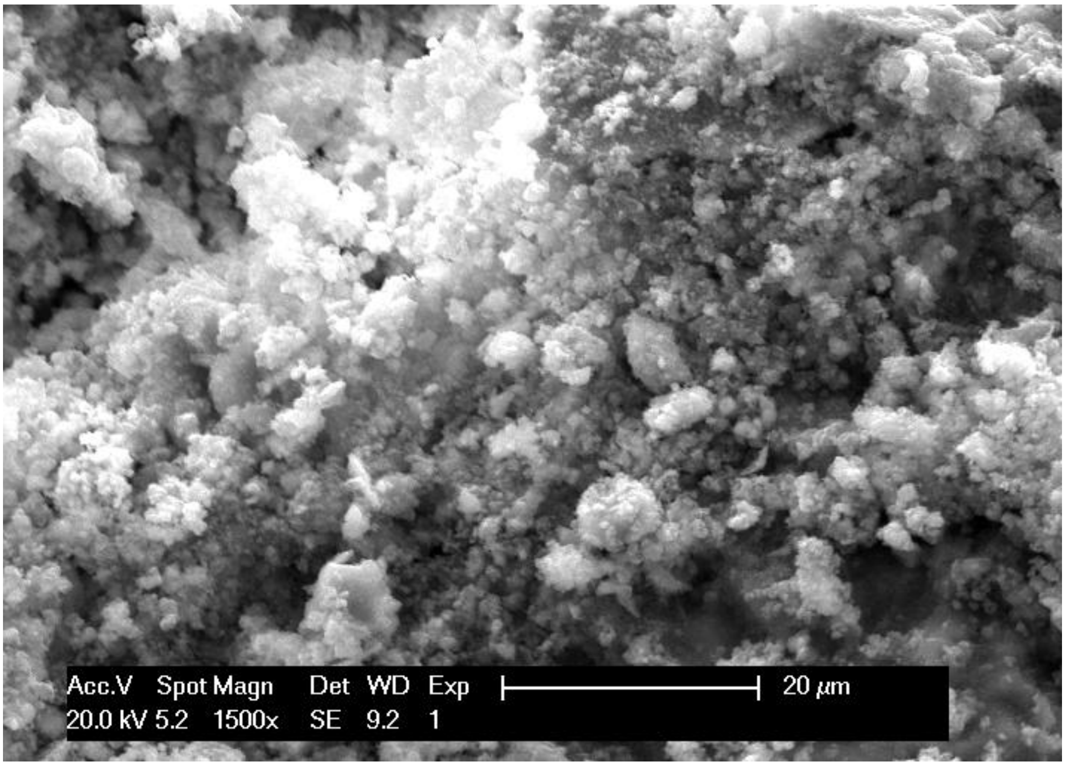


Figure B.55: SEM image of control specimen at 7 days (33-90)

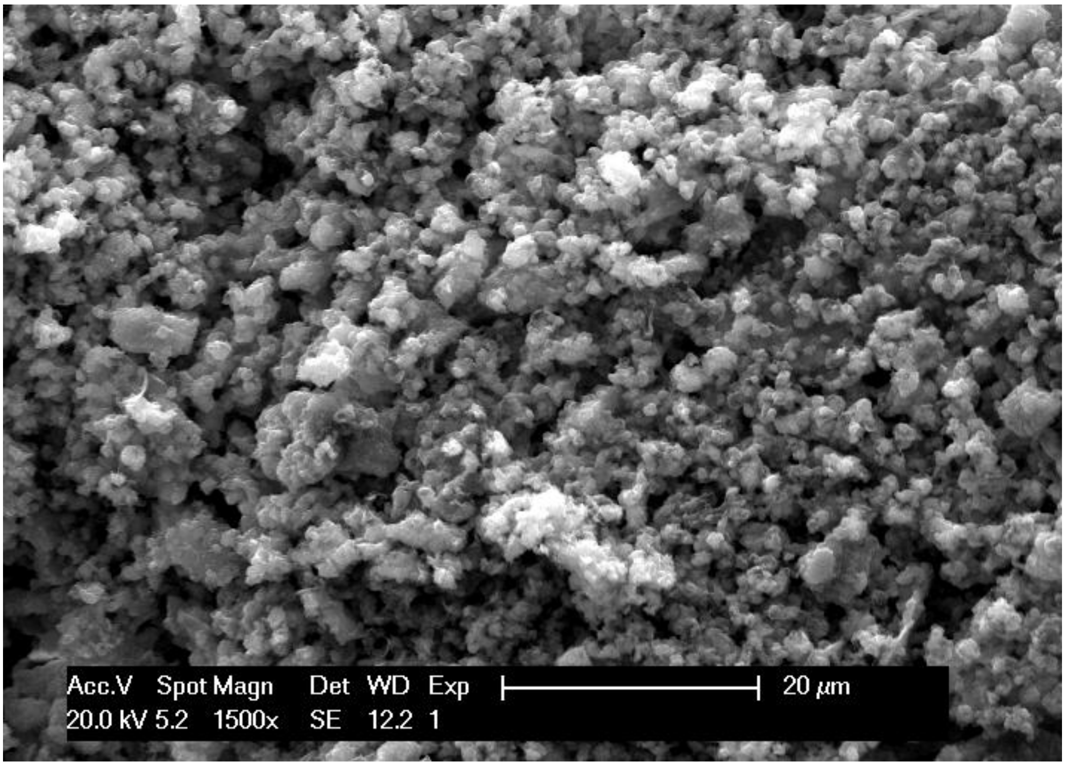


Figure B.56: SEM image of control specimen at 28 days (33-90)

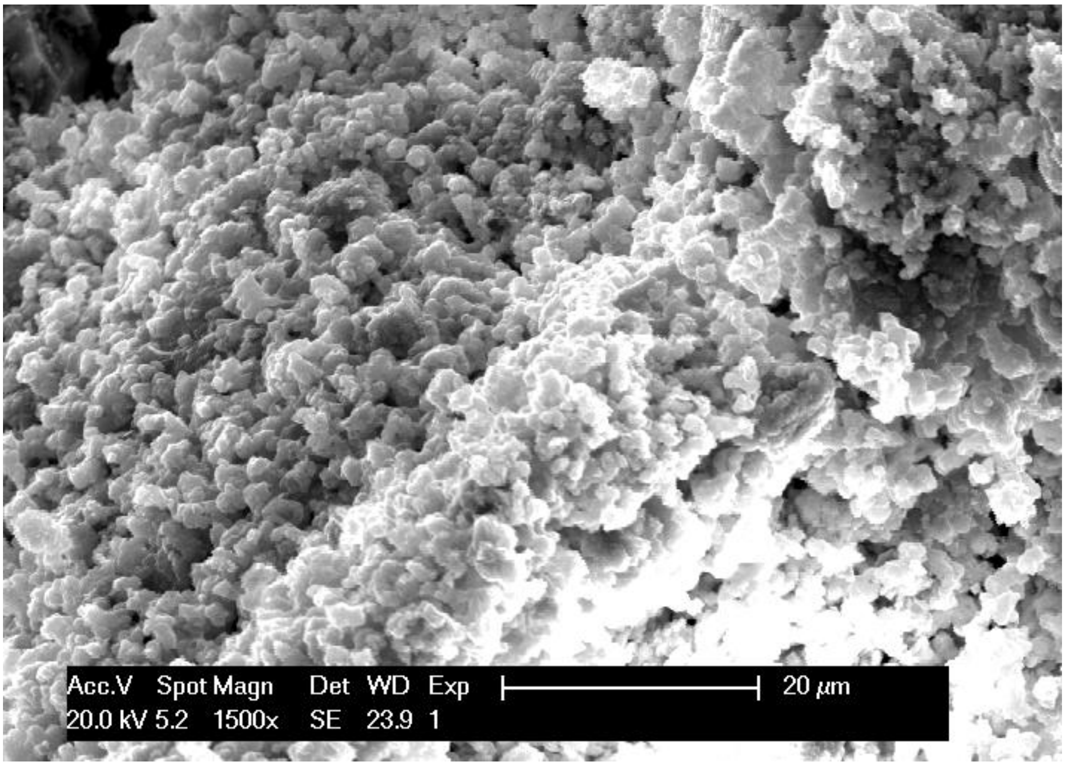


Figure B.57: SEM image of control specimen at 56 days (33-90)

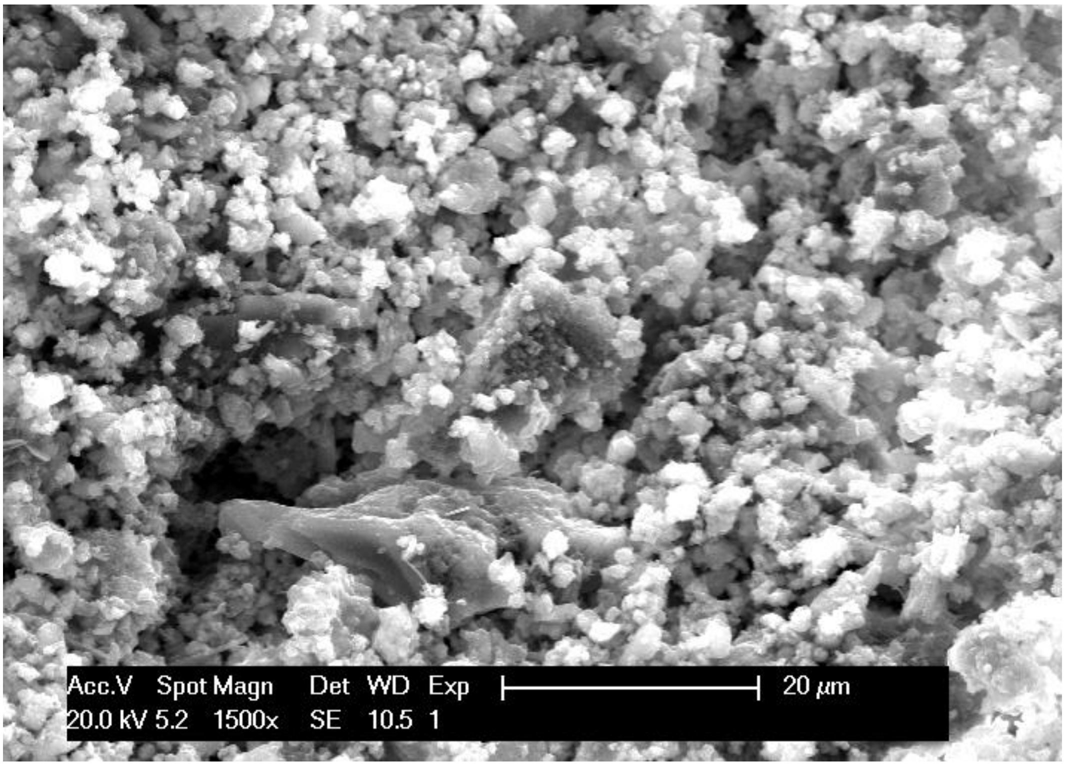


Figure B.58: SEM image of lime mortar with 6% oyster shells at 7 days (33-90)

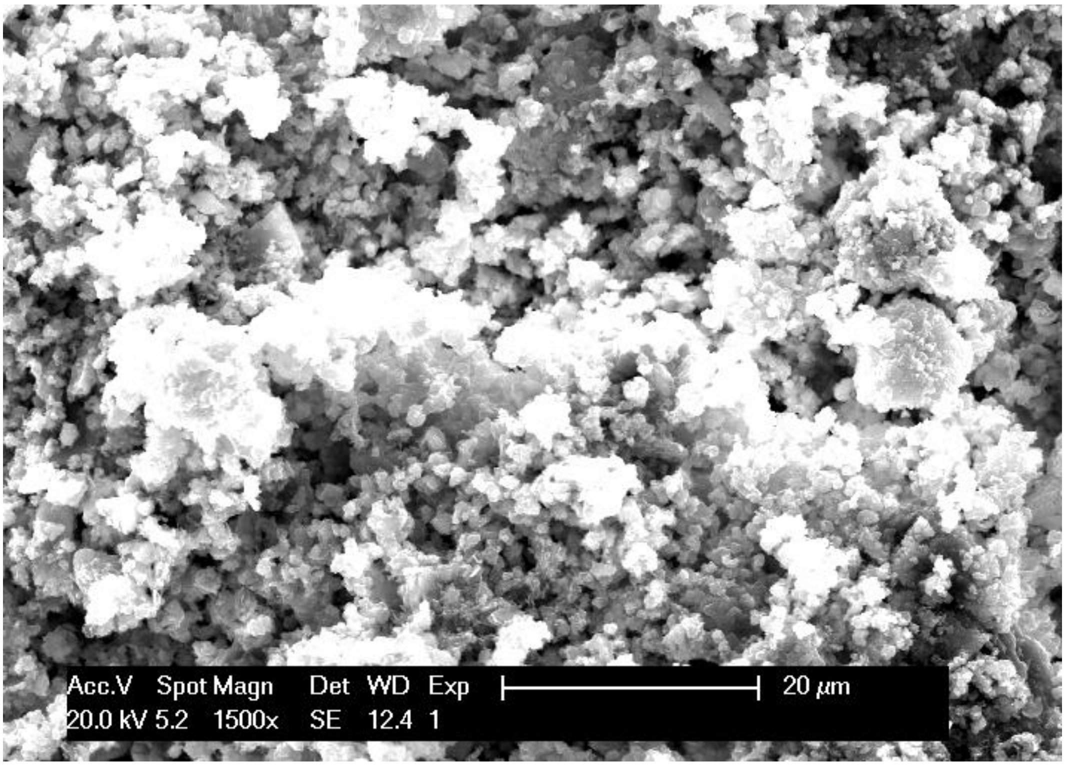


Figure B.59: SEM image of lime mortar with 6% oyster shells at 28 days (33-90)

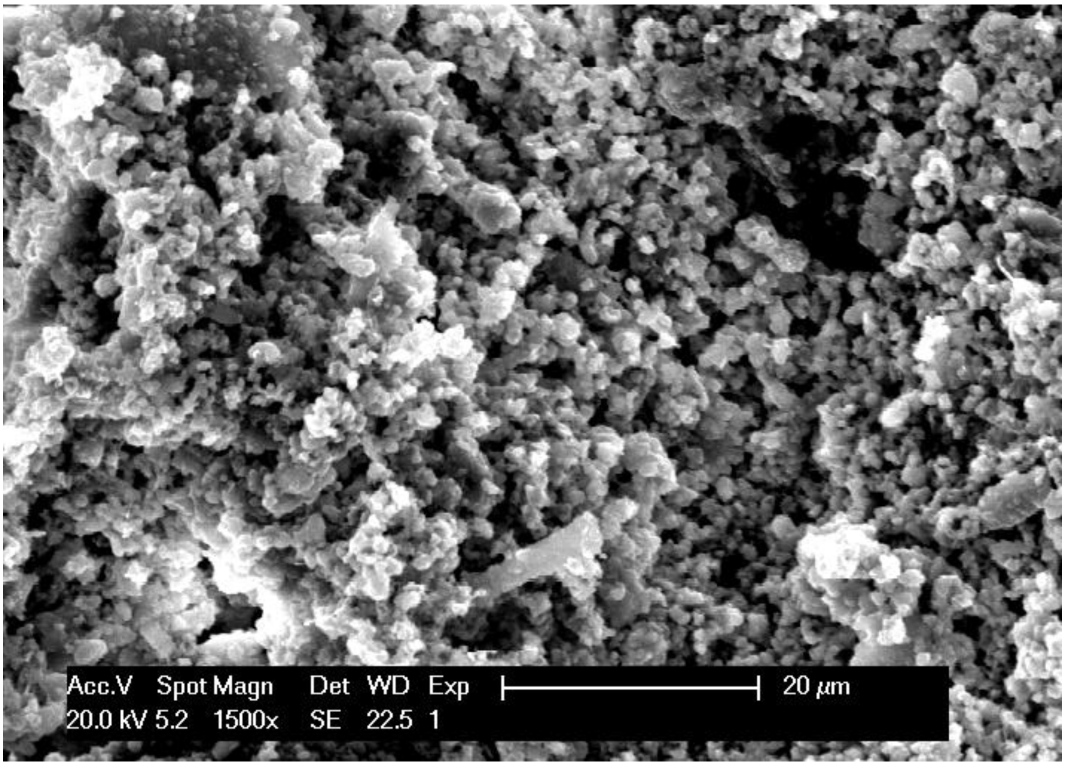


Figure B.60: SEM image of lime mortar with 6% oyster shells at 56 days (33-90)

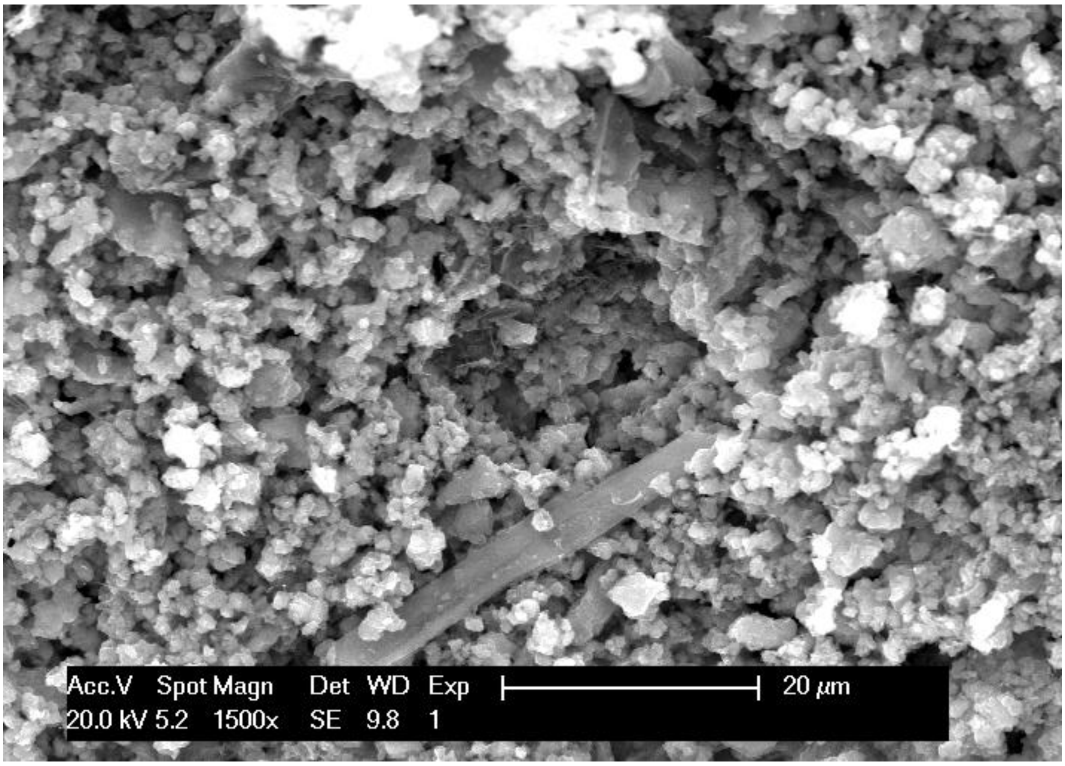


Figure B.61: SEM image of lime mortar with 10% oyster shells at 7 days (33-90)

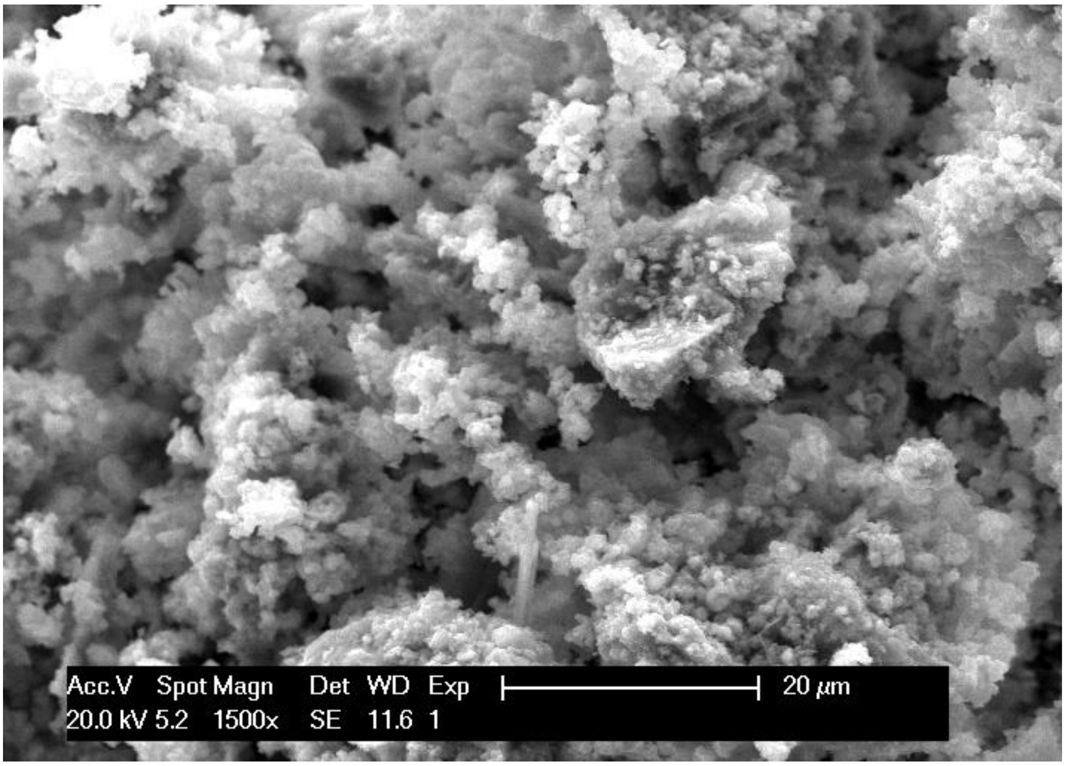


Figure B.62: SEM image of lime mortar with 10% oyster shells at 28 days (33-90)

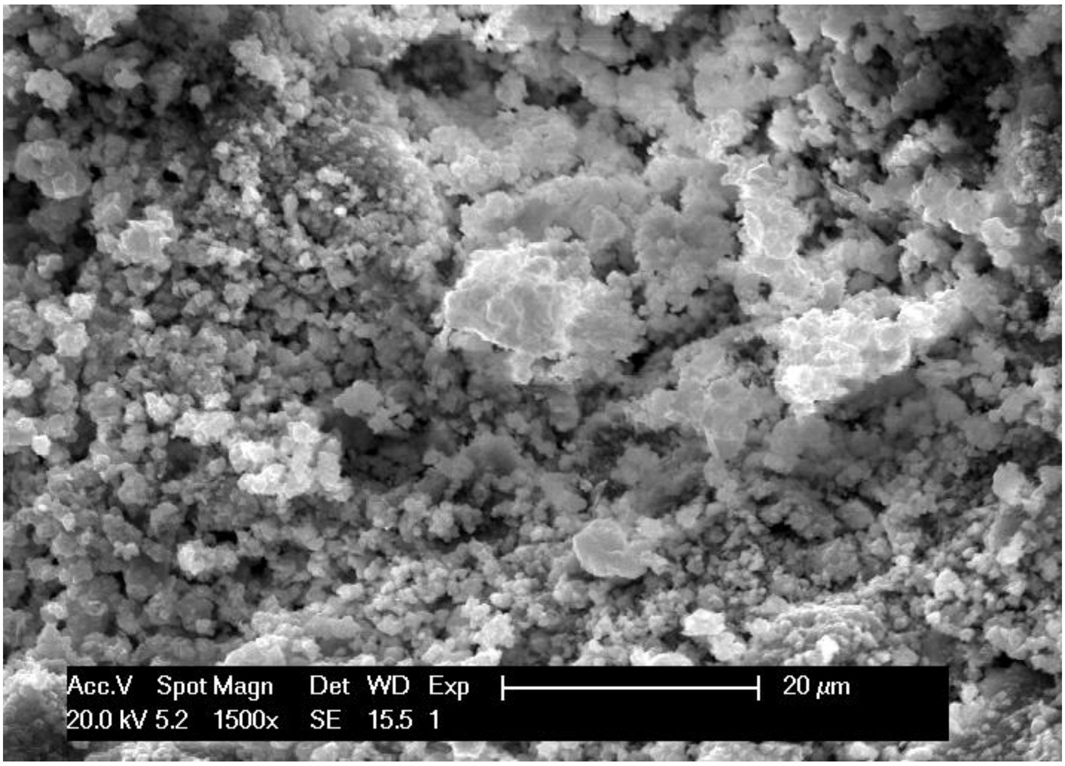


Figure B.63: SEM image of lime mortar with 10% oyster shells at 56 days (33-90)

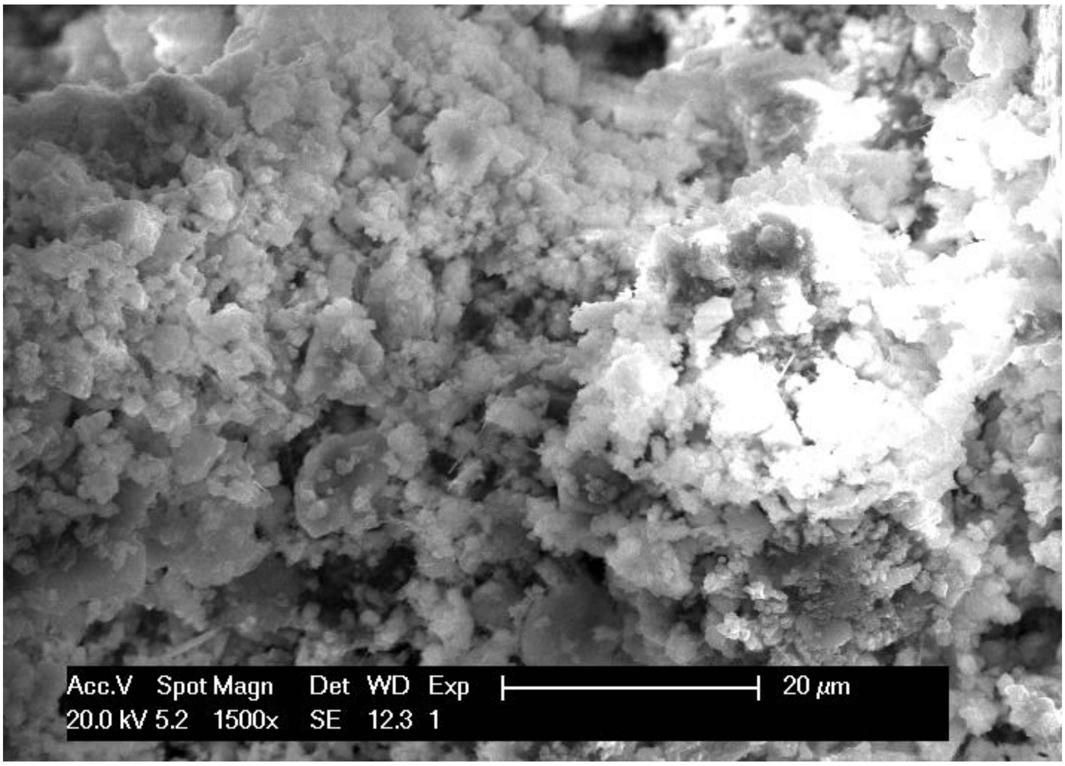


Figure B.64: SEM image of lime mortar with % limestone at 7 days (33-90)

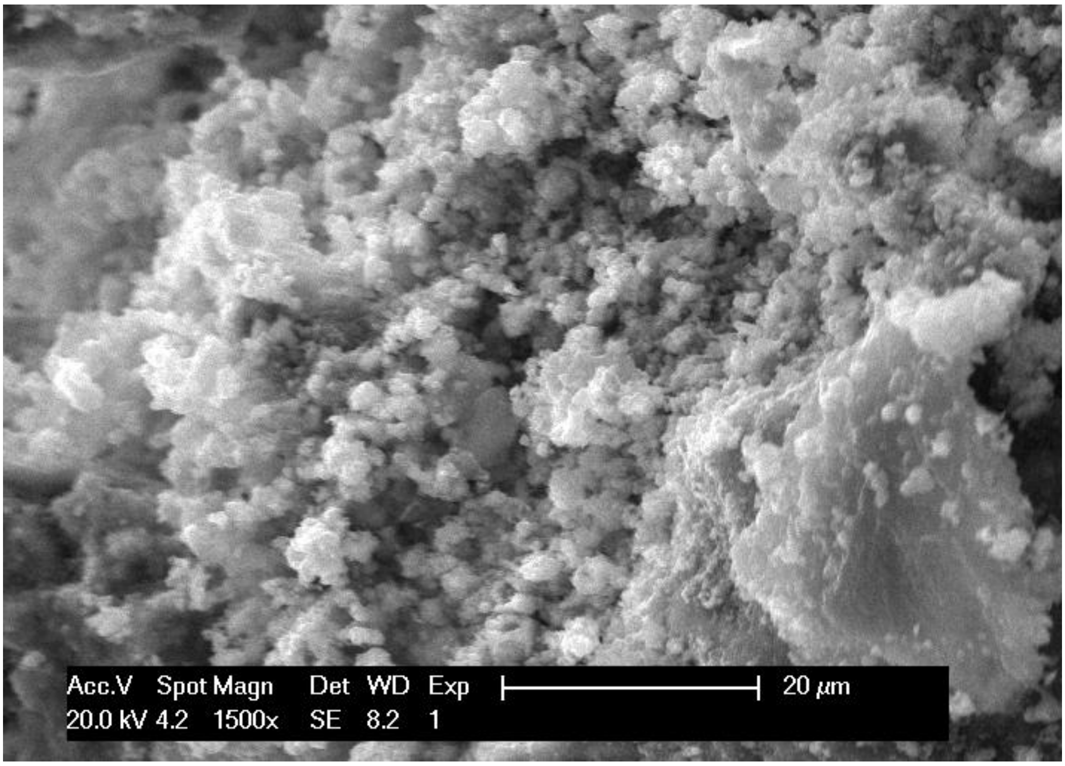


Figure B.65: SEM image of lime mortar with 6% limestone at 28 days (33-90)

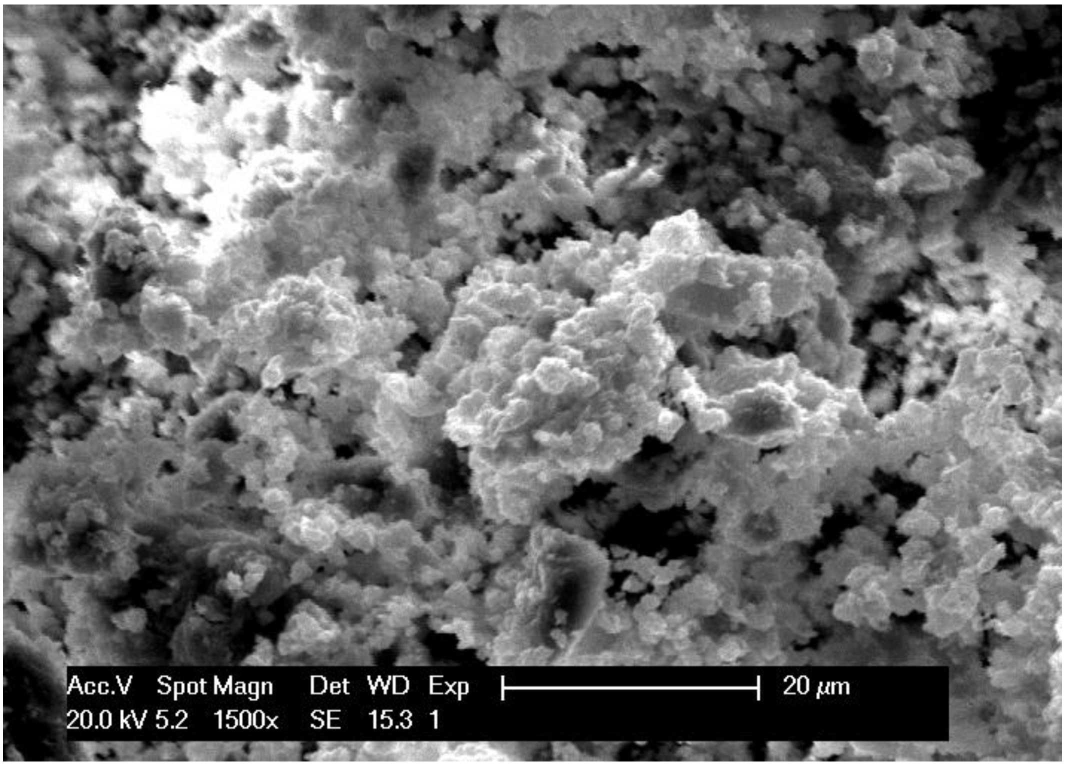


Figure B.66: SEM image of lime mortar with 6% limestone at 56 days (33-90)

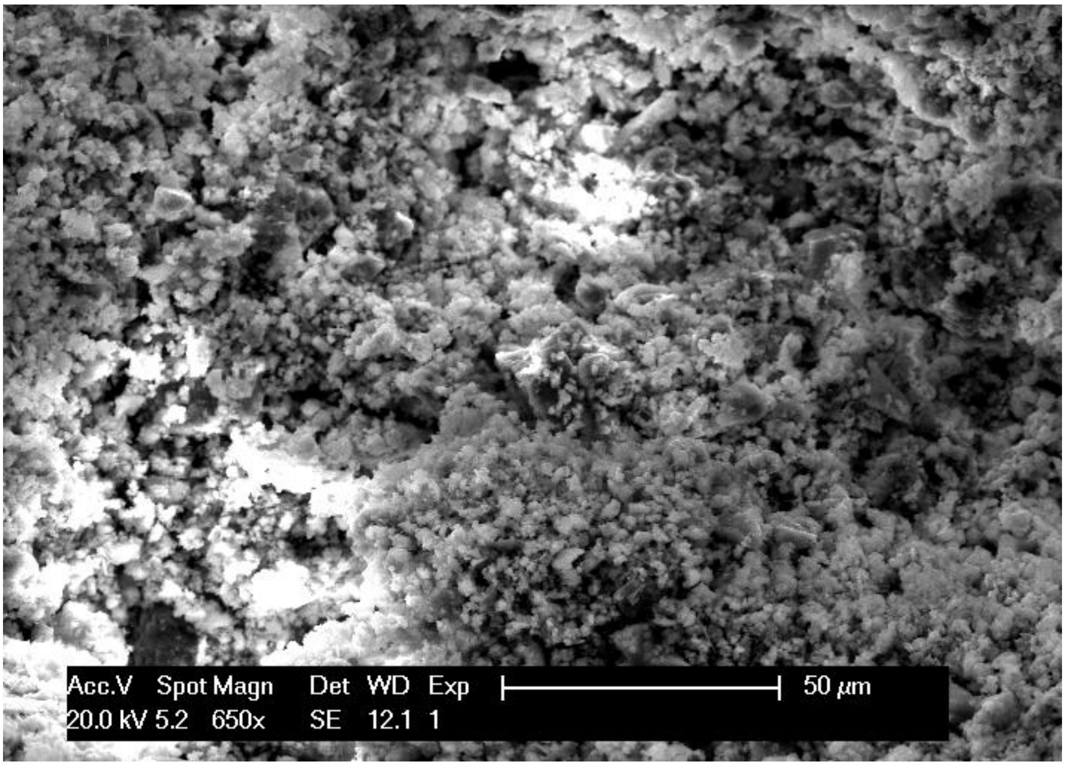


Figure B.67: SEM image of lime mortar with 10% limestone at 56 days (33-90)

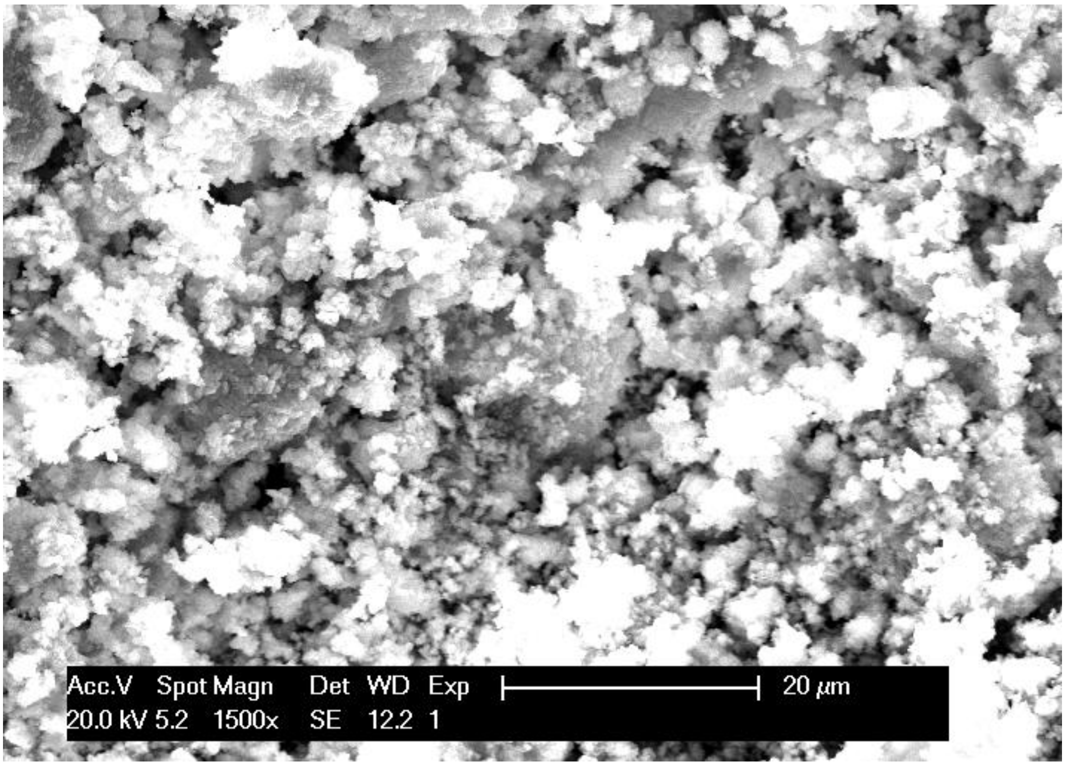


Figure B.68: SEM image of lime mortar with 10% limestone at 56 days (33-90)

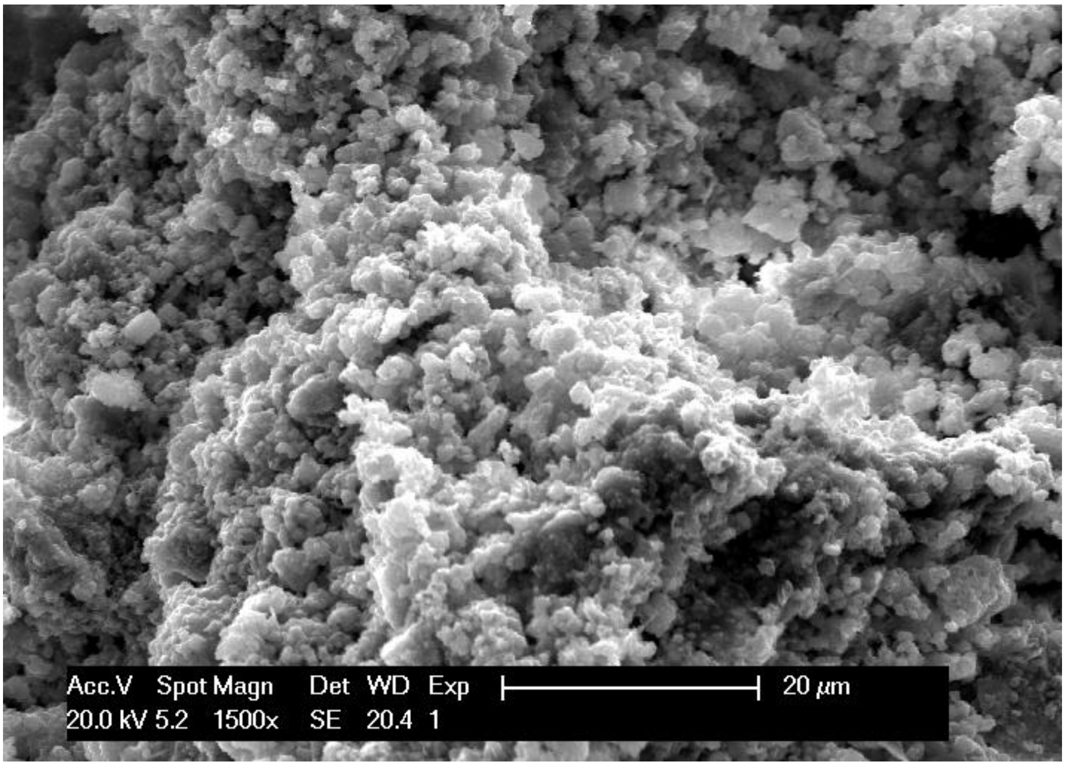


Figure B.69: SEM image of lime mortar with 10% limestone at 56 days (33-90)

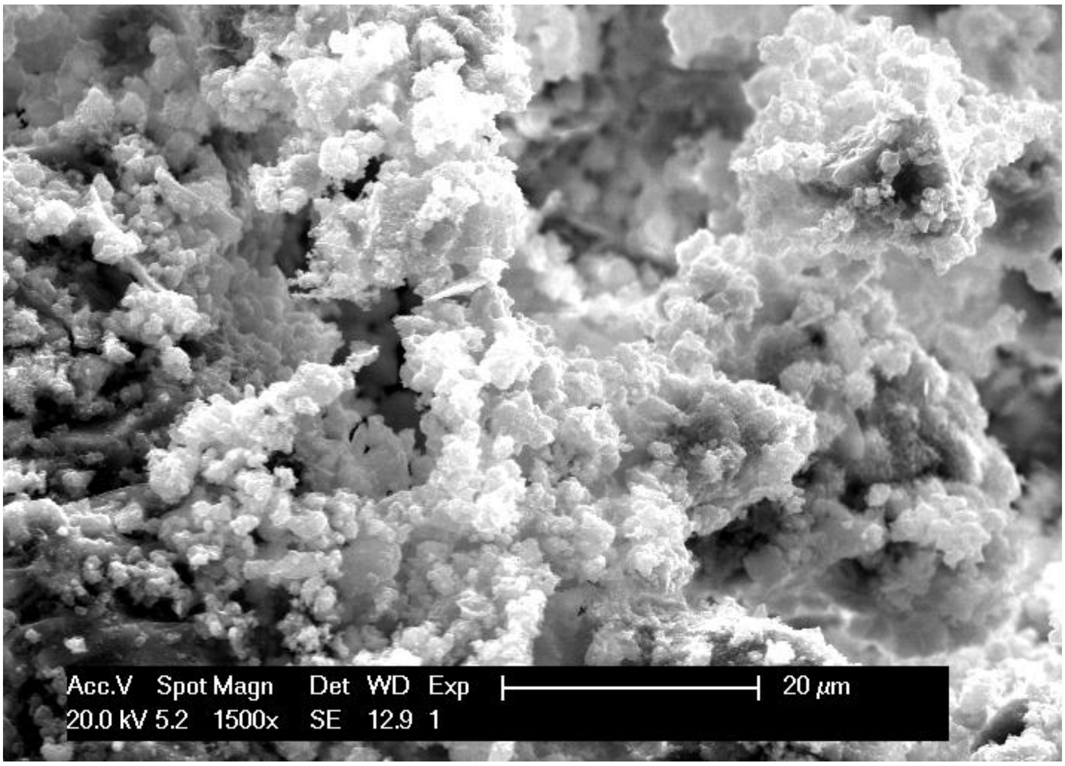


Figure B.70: SEM image of lime mortar with 6% marble at 7 days (33-90)

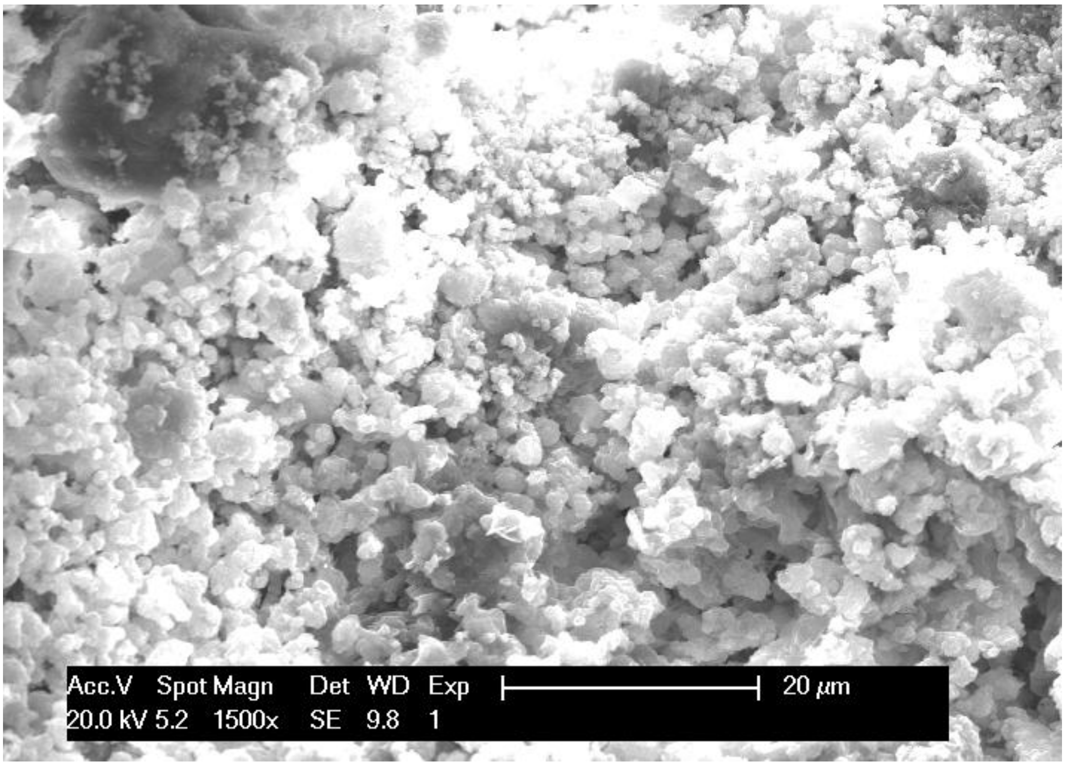


Figure B.71: SEM image of lime mortar with 6% marble at 28 days (33-90)

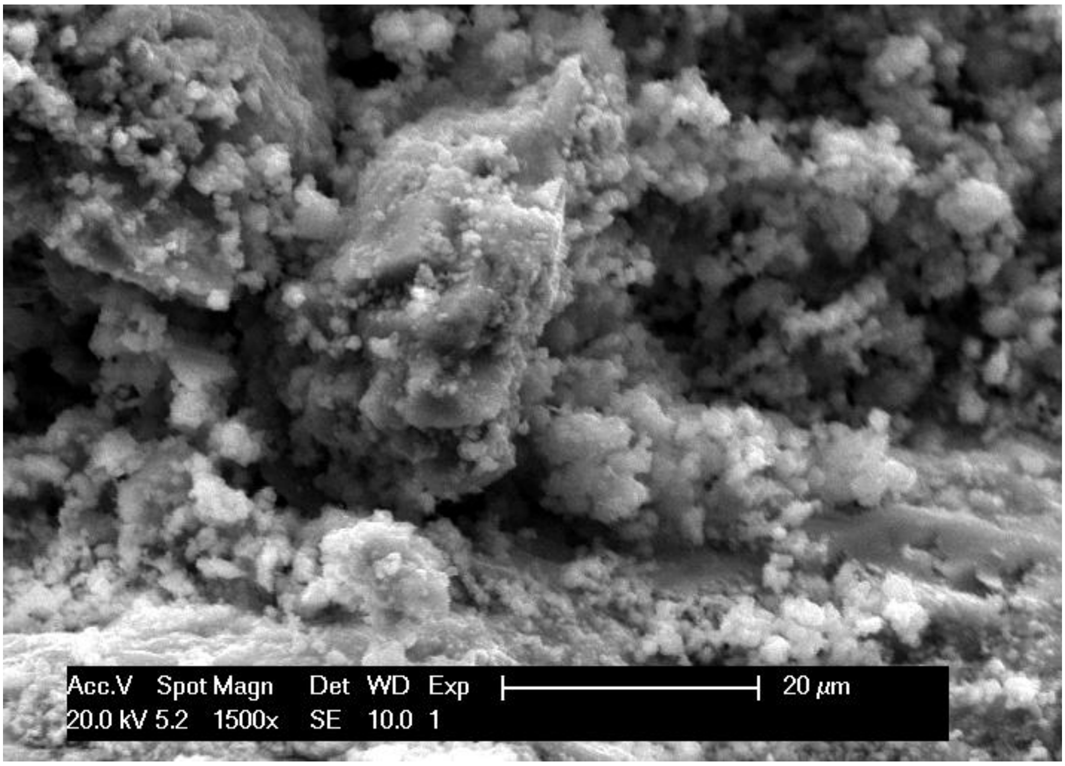


Figure B.72: SEM image of lime mortar with 6% marble at 56 days (33-90)

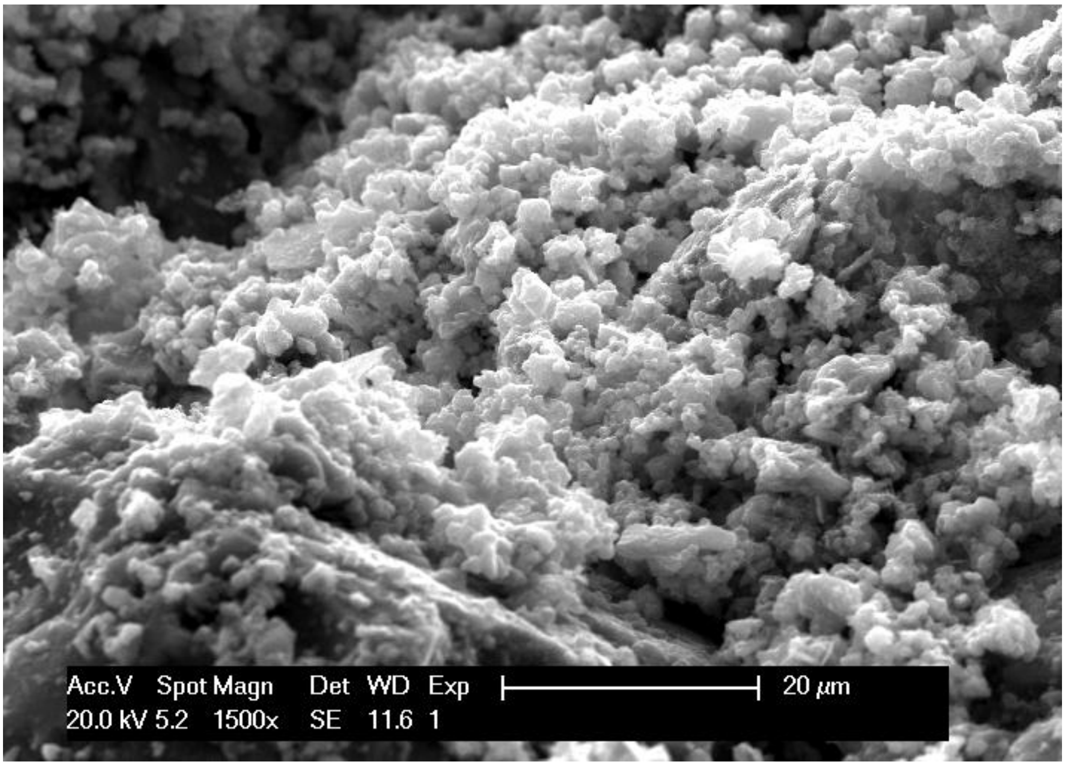


Figure B.73: SEM image of lime mortar with 10% marble at 7 days (33-90)

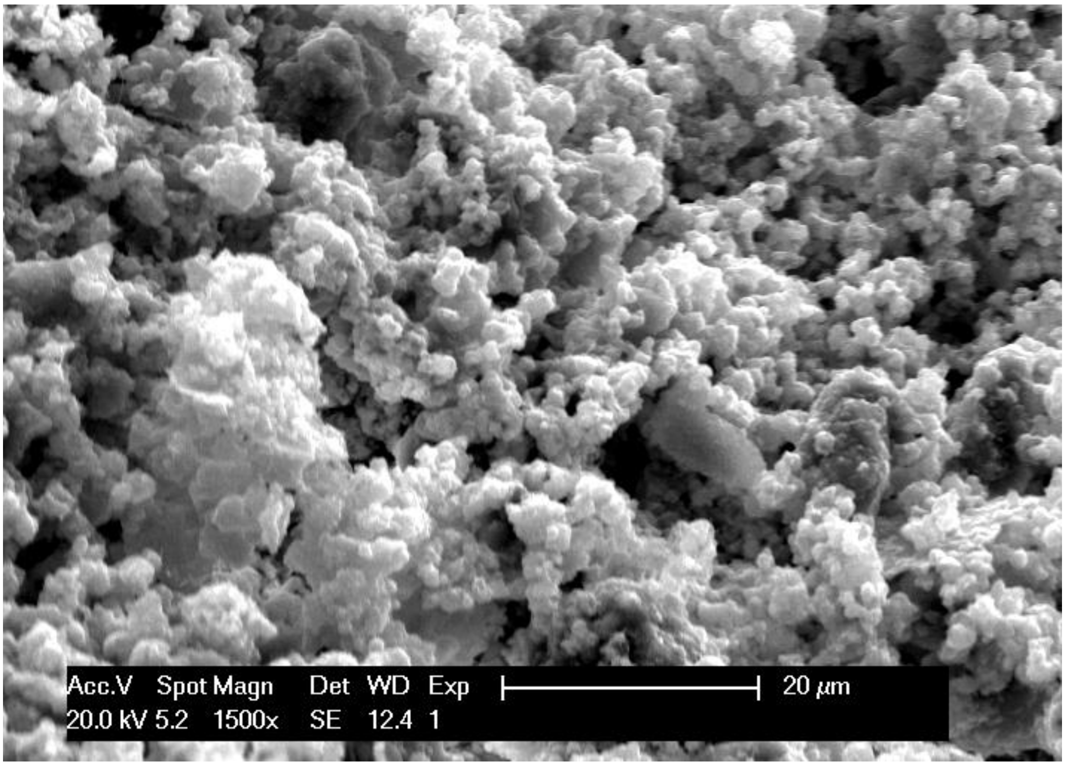


Figure B.74: SEM image of lime mortar with 10% marble at 28 days (33-90)

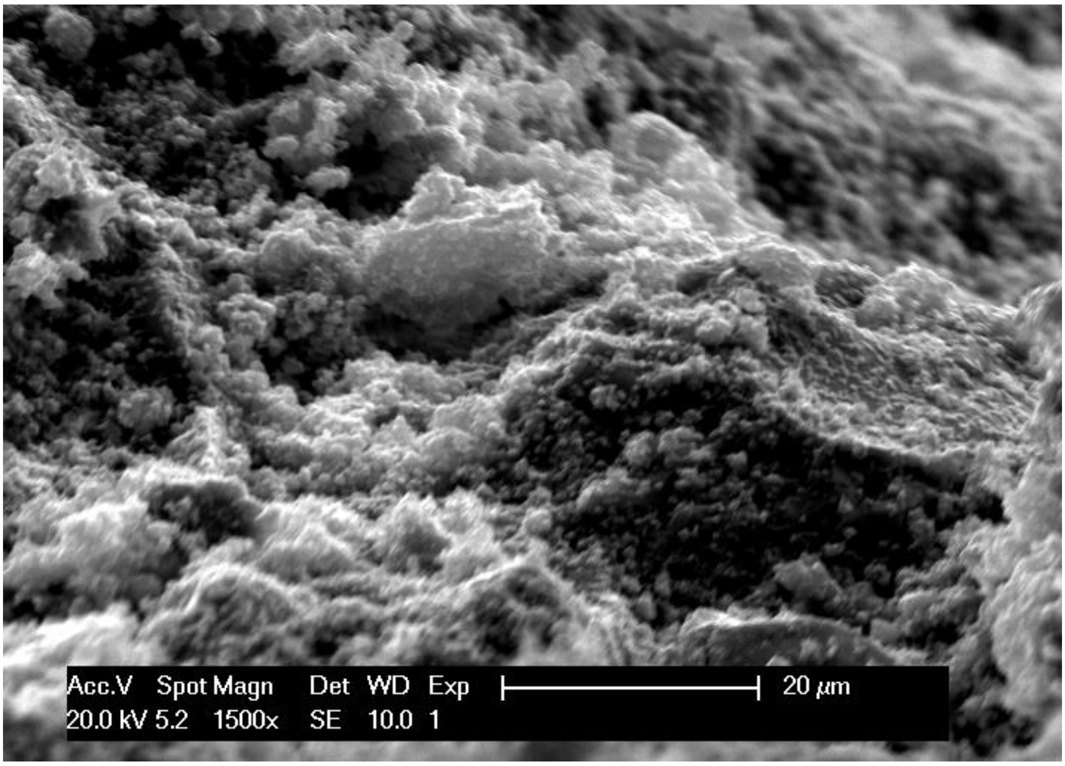


Figure B.75: SEM image of lime mortar with 10% marble at 56 days (33-90)

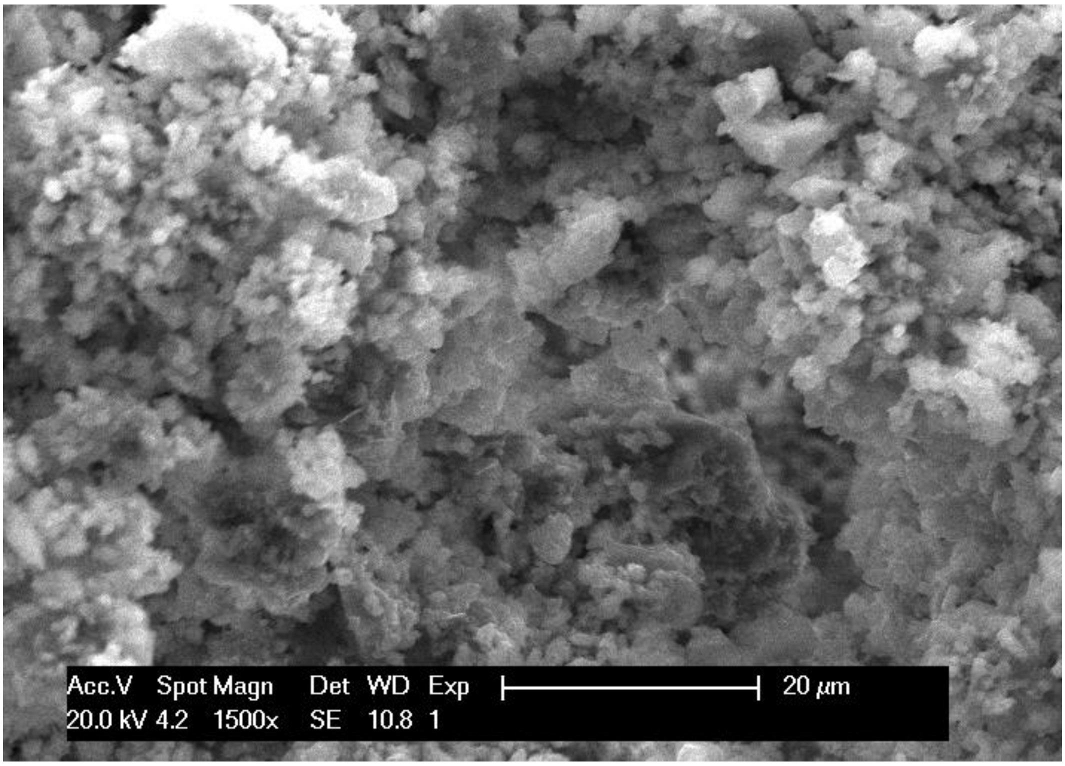


Figure B.76: SEM image of lime mortar with 6% precipitated $CaCO_3$ at 7 days (33-90)

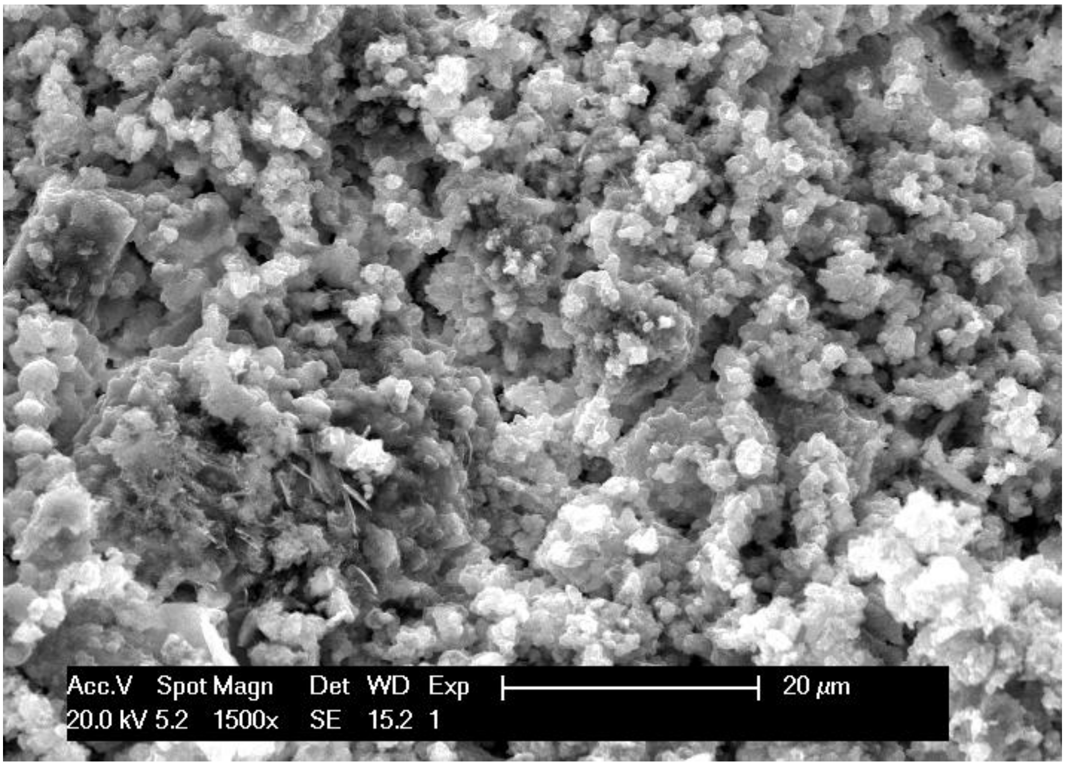


Figure B.77: SEM image of lime mortar with 6% precipitated $CaCO_3$ at 28 days (33-90)

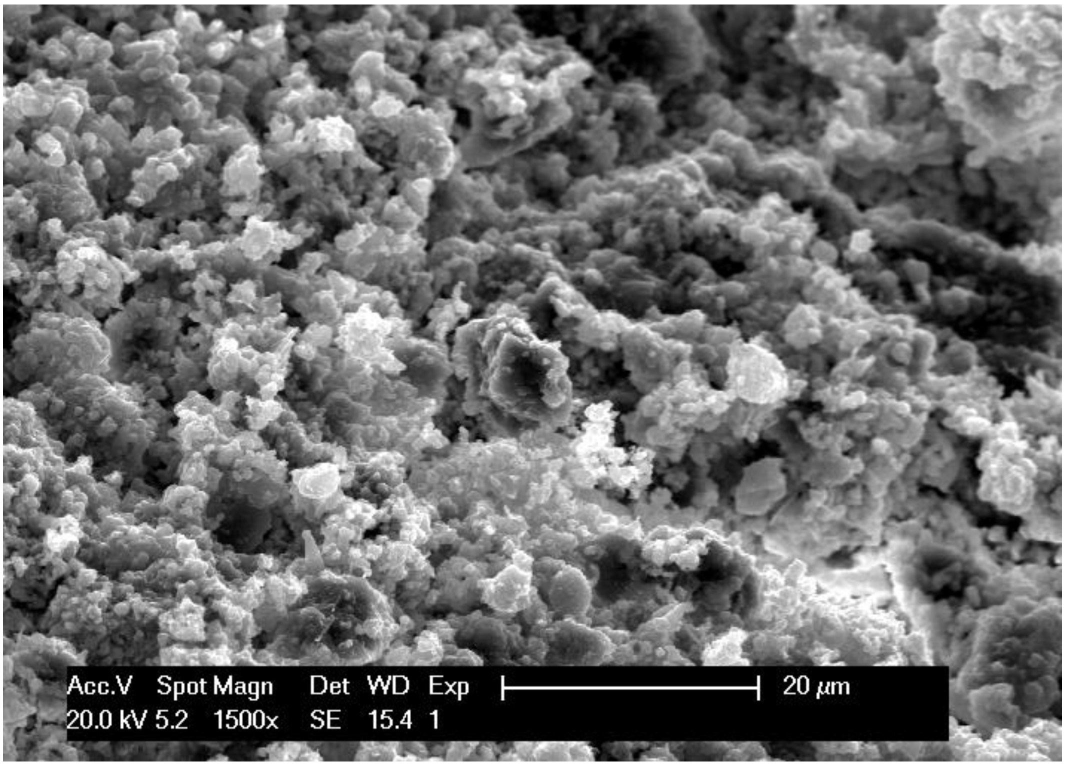


Figure B.78: SEM image of lime mortar with 6% precipitated $CaCO_3$ at 56 days (33-90)

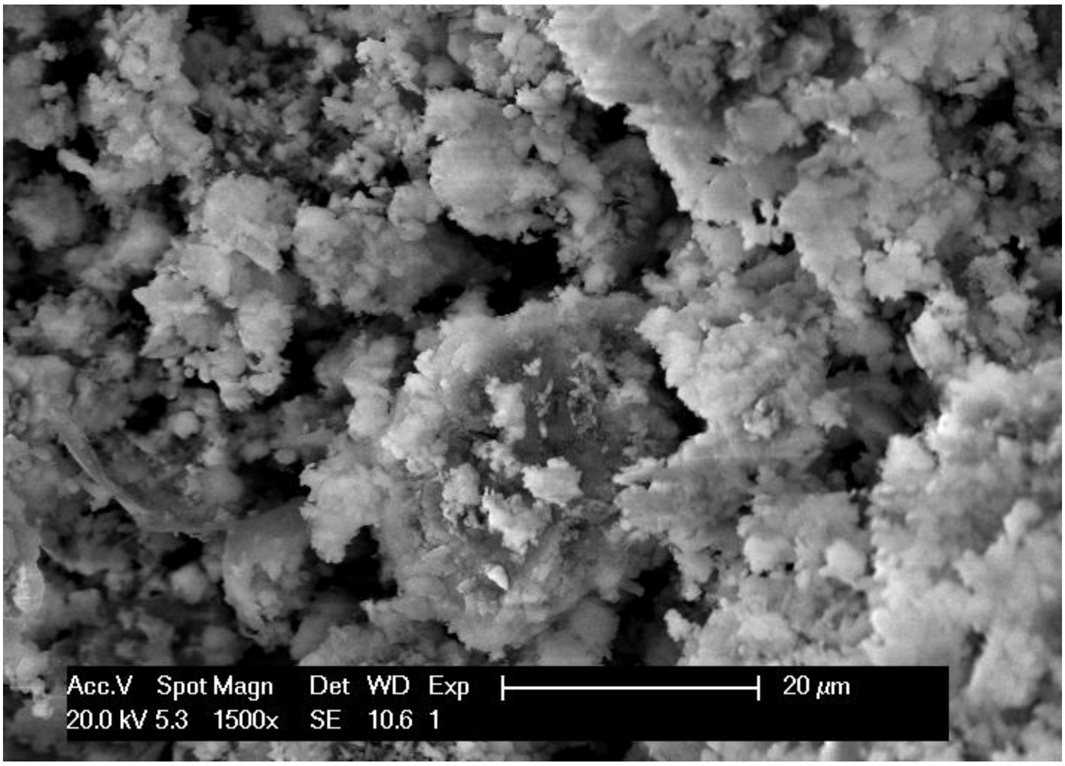


Figure B.79: SEM image of lime mortar with 10% precipitated $CaCO_3$ at 7 days (33-90)

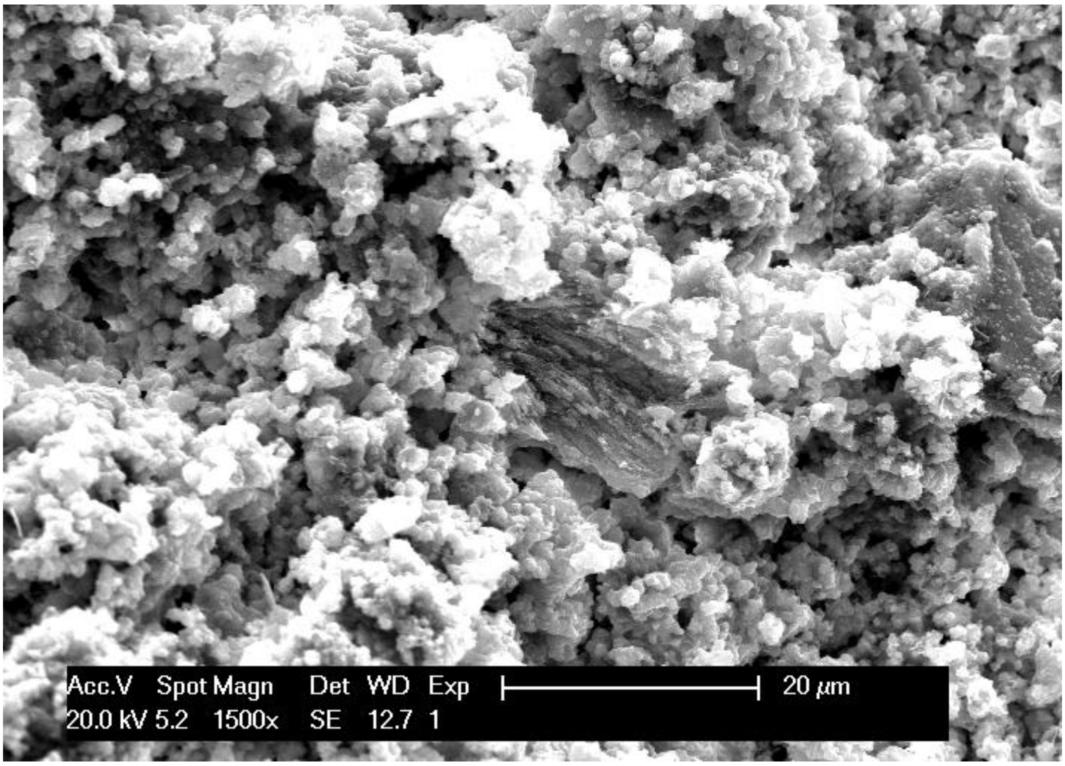


Figure B.80: SEM image of lime mortar with 10% precipitated $CaCO_3$ at 28 days (33-90)

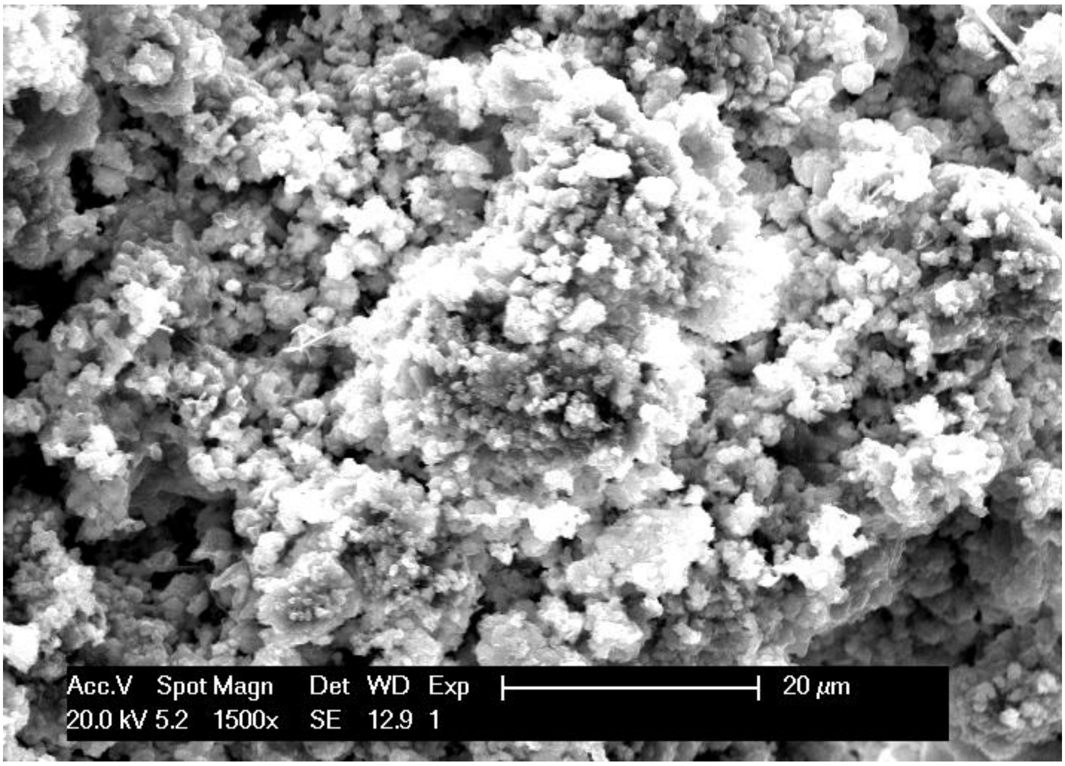


Figure B.81: SEM image of lime mortar with 10% precipitated $CaCO_3$ at 56 days (33-90)

Appendix C: Water Absorption of Mortar Specimens

Table C.1: Water absorption of mortar specimens cured in 20°C - 60% RH

Calcitic Filler	Seeding (%)	Age (day)	Water absorption (g/m^2)					
			Time (min)					
			1	3	5	10	15	30
Control	0	7	1875	3438	4688	5938	7500	10313
		14	2500	4063	5625	7813	9375	13125
		28	2500	4375	5625	7813	9688	13438
		42	2500	4375	5625	5625	8125	9375
		56	625	1875	3125	5000	6875	10625
Oyster shells	6	7	1875	3438	4688	6563	8438	11563
		14	2188	3750	4688	6875	8438	11563
		28	1875	3438	4688	6875	8750	12500
		42	2500	4375	5625	8125	9375	13125
		56	1875	2500	3750	5625	6875	10625
Oyster shells	10	7	1875	2813	3750	5625	7188	10000
		14	1875	3438	4375	6250	7813	10625
		28	2500	4063	5000	6875	8125	11250
		42	2500	4375	5625	8125	10000	13750
		56	1875	2500	3750	6250	8125	11875
Limestone	6	7	3125	4375	5625	8125	13125	13438
		14	2500	4375	5313	7813	9375	12813
		28	2500	4375	5313	7500	9063	13125
		42	3750	5625	7500	10000	11875	15625
		56	3125	4375	5625	8125	10000	13750
Limestone	10	7	1875	2813	3438	5625	7500	10938
		14	1875	2813	3750	5625	6875	10000
		28	3438	5000	6250	5625	10313	14063
		42	1875	3750	4375	6875	8125	12500
		56	2500	3750	4375	7500	8125	11250
Marble	6	7	1250	2813	3438	5122	6528	9600
		14	2188	3438	4688	6563	7813	11250
		28	1875	3438	4375	6250	8125	11250
		42	3125	5000	5625	8125	9375	12500
		56	1875	3125	3750	6250	7500	11250
Marble	10	7	2500	4063	5313	7656	9294	12653
		14	1250	2188	3125	5000	6250	9375
		28	2813	4688	5938	7813	9063	12813
		42	3750	5000	5625	8125	9375	13125
		56	2500	3750	4375	6875	8750	11875
Precipitated $CaCO_3$	6	7	1875	3438	4375	6372	7875	10959
		14	1875	2813	3750	5625	7188	10625
		28	938	2188	3438	5313	7188	10938

		42	3125	5000	6250	8125	9375	12500
		56	2500	3750	5000	6875	8750	11875
Precipitated $CaCO_3$	10	7	2500	4063	5313	7059	8372	11225
		14	2500	3750	4688	6563	8125	10625
		28	2813	4063	5000	6875	8125	11250
		42	2500	3750	4375	6250	7500	10000
		56	1875	2500	3750	5000	6250	9375

Table C.2: Water absorption of mortar specimens cured in 27°C-90%RH

Calcitic Filler	**Seeding (%)**	**Age (day)**	**Water absorption (g/m^2)**					
			Time (min)					
			1	**3**	**5**	**10**	**15**	**30**
Control	0	7	8119	10119	11663	14456	16544	21144
		14	5397	7347	8922	11794	13975	16169
		28	3691	5678	7009	9509	11344	15406
		42	4356	6494	7859	18669	11925	15575
		56	3750	5625	6875	8750	10625	14375
Oyster	6	7	4584	5753	6447	7922	8919	10784
		14	3438	4944	5756	6988	8044	10313
		28	4069	5600	6481	7850	9063	11713
		42	3753	5272	6119	7419	8553	11013
		56	4181	5344	6456	8250	9656	13319
Oyster	10	7	3716	5116	6078	7875	9238	12191
		14	2981	4738	5638	7244	8650	11369
		28	3288	4775	5825	7738	9181	12056
		42	3134	4756	5731	7491	8916	11713
		56	3219	4638	5675	7531	8931	11994
Limestone	6	7	2500	4206	5481	8169	9769	13900
		14	3619	6244	7431	10038	11856	15844
		28	4038	6419	7544	9969	11694	15250
		42	3828	6331	7488	10003	11775	15547
		56	3681	4963	6275	8269	9913	14094
Limestone	10	7	3363	4513	5331	7113	8138	10413
		14	3881	6163	7319	9344	10881	14194
		28	4781	6938	8156	10238	11894	15525
		42	4331	6550	7738	9791	11388	14859
		56	3381	4475	5538	7156	8413	11619
Marble	6	7	2063	4066	4688	6797	8213	11213
		14	3375	4850	5900	7838	8963	11844
		28	3600	5006	6025	7750	9088	11688
		42	3488	4928	5963	7794	9025	11766
		56	4331	6188	7475	9825	11544	15281
Marble	10	7	4938	6491	7034	8881	10113	12928
		14	5563	7244	8450	10581	12325	14313
		28	6138	7631	8838	10981	12738	16619
		42	5850	7438	8644	10781	12531	15466

		56	5175	6925	8200	10675	12406	16106
Precipitated $CaCO_3$	6	7	3316	4700	5722	7494	8659	11488
		14	1250	3125	3750	5625	6875	8750
		28	2500	3125	4375	6250	7500	8750
		42	1875	3125	4063	5938	7188	8750
		56	4350	5369	6319	8244	9456	11938
Precipitated $CaCO_3$	10	7	2450	3963	5263	7688	9563	13719
		14	2500	3750	5000	6875	8125	10000
		28	2500	3750	5000	6875	8125	10000
		42	2500	3750	5000	6875	8125	10000
		56	3125	4375	5000	6875	8125	11250

Table C.3: Water absorption of mortar specimens cured in 33°C-90%RH

Calcitic Filler	Seeding (%)	Age (day)	Water absorption (g/m^2)					
			Time (min)					
			1	3	5	10	15	30
Control	0	7	4846	6965	8500	11240	13571	16967
		14	4063	6725	8713	12013	14638	19944
		28	4394	6913	8825	12038	14606	17931
		42	4706	7106	9056	12181	15025	20831
		56	4388	6915	8865	12077	14756	19569
Oyster shells	6	7	6725	8806	10838	14513	17281	21081
		14	6081	8581	10456	13994	16731	19331
		28	6925	9588	11575	15219	18025	20875
		42	6577	8992	10956	14575	17346	20429
		56	5088	7919	9644	12950	15338	18831
Oyster shells	10	7	4902	6279	7523	9738	11475	15092
		14	5044	7019	8613	10975	12881	16469
		28	1375	3300	4838	7100	8913	12281
		42	5356	7469	9150	11644	13619	18413
		56	3925	5929	7533	9906	11804	15721
Limestone	6	7	3888	5569	6788	9038	10675	14631
		14	10581	12269	13538	15738	17344	21194
		28	4606	6231	7450	9588	11256	15325
		42	6358	8023	9258	11454	13092	17050
		56	4250	6213	7194	9244	10756	14088
Limestone	10	7	4408	6546	8102	10894	13031	17379
		14	4125	6350	7794	10413	12188	16281
		28	4763	7031	8525	11294	13150	17413
		42	5019	7250	8688	10575	12544	16869
		56	4635	6877	8335	10760	12627	16854
Marble	6	7	5469	7717	9367	12265	14321	16967
		14	5781	7775	9156	11500	13369	16663
		28	6788	8694	10038	12388	14219	15856
		42	4488	5719	6713	8238	9513	12450
		56	4206	5425	6250	7913	9169	12075

Marble	10	7	5202	6844	8025	10185	11931	14181
		14	6106	8075	9550	12319	14369	20450
		28	6663	8869	10456	13269	15394	23531
		42	3175	5119	6006	7869	9256	12450
		56	4275	5625	6725	8675	10219	13594
Precipitated $CaCO_3$	6	7	3681	5744	7513	9725	11581	15050
		14	1819	3806	7138	9275	11088	14944
		28	6244	7931	14250	16450	18344	22438
		42	3915	5827	9633	11817	13671	17477
		56	3844	5281	6581	8569	10163	13713
Precipitated $CaCO_3$	10	7	4967	5871	6783	8531	9942	12344
		14	3613	5888	7381	9631	11531	15769
		28	4294	6519	8025	10375	12288	15663
		42	4044	6025	7419	9656	11456	15238
		56	3983	6144	7608	9888	11758	15556

LIST OF REFERENCES

AFP (2012) 'Tropical citizens die 7.7 years sooner', [online], available: [Accessed 24 March 2014 2014].

Ahmad, A. G. (2004) 'The Dilapidation Survey Report: Understanding Common Building Defects', *Majalah Akitek*, 3.

Ahrens, C. D. (2013) *Meteorology Today,* Australia: Cengage Learning Ltd.

Al-Ani, S. H. and Al-Zaiwary, M. A. K. (1988) 'The effect of curing period and curing delay on concrete in hot weather', *Materials and Structures*, 21(3).

Al-Defai, N. (2013) *The Consequences of the Dewatering of Freshly-Mixed Wet Mortars by the Capillary Suction of Brick Masonry*, unpublished thesis University of Manchester.

Al-Khaiat, H., Haque, M. N. and Fattuhi, N. (2004) 'Concrete Carbonation in Arid Climate', in *29th Conference on Out World in Concrete & Structure*, Singapore, Singapore Concrete Institute,

Ali, H. H. and Al Nsairat, S. F. (2009) 'Developing a green building assessment tool for developing countries – Caseof Jordan', *Building and Environment,* 44(5), 1053-1064.

Aligizaki, K. K. (2006) *Pore Structure of Cement-based Materials,* Oxford, UK: Taylor & Francis.

Allen, E. and Iano, J. (2009) *Fundamental of Building Construction: Materials and Methods,* 5th ed., New Jersey, USA: John Wiley & Sons.

Allen, G. (2003) *Hydraulic lime mortar for stone, brick and block masonry,* Shaftesbury: Donhead.

Allen, G., Allen, J., Elton, N., Farey, M., Holmes, S., Livesey, P. and Radonjic, M. (2003) *Hydraulic Lime Mortar for Stone, Brick and Block Masonry,* Dorset, UK: Donhead Publishing Ltd.

Almusallam, A., Al-Gahtani, A., Aziz, A. and Dakhil, F. (1996) 'Effect of Reinforcement Corrosion on Flexural Behaviour of Concrete Slabs', *Materials in Civil Engineering,* 8(3), 123-127.

Alsheikh, S. A. (2013) 'Study of Sorptivity of Self-Compacting Concrete with Different Chemical Admixtures ', *Concrete Research Letters,* 4(3), 639-655.

Appels, W. M. (2013) *Water Redistribution at the Soil Surface: Ponding and Surface Run-off In Flat Areas,* unpublished thesis Wageningen University.

Arnold, R. (2003) *Working with Concrete,* Connecticut, USA: The Taunton Press.

Aruntaş, H. Y., Gürü, M., Dayı, M. and Tekin, I. (2010) 'Utilization of waste marble dust as an additive in cement production', *Materials & Design,* 31(8), 4039-4042.

Ashurst, J. (2002) *Mortars, plasters and renders in conservation,* 2nd ed., [London]: Ecclesiastical Architects' and Surveyors' Association.

Astier, S. (2006) 'Physical & Mechanical Data of St Astier Natural Hydraulic Limes ', [online], available: [Accessed 25 February 2012 2012].

Azar, C., Lindgren, K. and Larson, E. D. (2006) *Carbon capture and storage from fossil fuels and biomass: costs and potential role in stabilizing the atmosphere,* London, UK: HM Treasury.

Badger, S. R., Tikalsky, P. J. and Scheetz, B. E. (2002) *Increased Durability Through Nano-Scale Seeding in Portland Cement,* Louisiana, USA: Louisiana Transportation Research Center.

Baechler, M. C. (2011) *40% Whole-House Energy Savings in the Hot-Humid Climate* Washington DC, USA: Pacific Northwest National Laboratory.

Bai, J., Wild, S. and Sabir, B. B. (2002) 'Sorptivity and strength of air-cured and water-cured PC–PFA–MK concrete and the influence of binder composition on carbonation depth', *Cement and Concrete Research,* 32(11), 1813-1821.

Bakharev, T., Sanjayan, J. G. and Cheng, Y. B. (1999) 'Effects of Elevated Temperature Curing on Properties of Alkali Activated Slag Concrete', *Cement & Concrete,* 29.

Ball, R. J., El-Turki, A. and Allen, G. C. (2009) *Influence Of Carbonation On The Load Dependant Deformation Of Hydraulic Lime Mortars,* translated by Bath, UK.

Ball, R. J., El-Turki, A. and Allen, G. C. (2010) 'Influence of carbonation on the load dependent deformation of hydrauliclime mortars', *Materials Science and Engineering: A,* 528(7-8).

Banfill, P. F. G. and Forster, A. M. (1999) 'A Relationship Between Hyraulicity And Permeability Of Hydraulic Lime' in BARTOS, P., GROOT, C. and HUGHES, J. J., eds., *Proceedings PRO012: International RILEM Workshop on Historic Mortars: Characteristics and Tests Paisley, Scotland,* Edinburgh. United Kingdom: RILEM, 11.

Barnes, M. W. and Scheetz, B. E. (1991) 'The chemistry of Al-tobermorite and its co-existing phases at 175C.', in Scheetz, B. E., ed. *Materials Research Society Symposia*, Pittsburgh, USA, Materials Research Society, 243-271.

Barrientos, M. and Soria, C. (2010) 'Hydraulic Cement: World Production', *United States Geological Survey Mineral Resource Program* [online], available: [Accessed 5 February 2014 2014].

Barros, M. C., Bello, P. M., Bao, M. and Torrado, J. J. (2009) 'From waste to commodity: transforming shells into high purity calcium carbonate', *Journal of Cleaner Production,* 17(3), 400-407.

Basheer, M., Concalves, A. F. and Torrent, R. (2007) 'Non-destructive Methods to Measure Water Transport' in Torrent, R. and Luco, L. F., eds., *Non-destructive Evaluation of the Concrete Cover,* France: RILEM Publications.

Battey, M. H. and Pring, A. (1997) *Mineralogy for Students,* 3rd ed., Essex, UK: Addison Wesley Longman Limited.

Behnood, A. and Ziari, H. (2008) 'Effects of silica fume addition and water to cement ratio on the properties of high-strength concrete after exposure to high temperatures', *Cement and Concrete Composites,* 30(2), 106-112.

Benachour, Y., Davy, C. A., Skoczylas, F. and Houari, H. (2008) 'Effect of a high calcite filler addition upon microstructural, mechanical, shrinkage andtransport properties of a mortar', *Cement and Concrete Research,* 38.

Benachour, Y., Davy, C. A., Skoczylas, F. and Houari, H. (2009) 'Effect of high calcite filler addition upon micro-structure and freeze/thaw resistance of a mortar' in Tanabe, T., Sakata, K., Mihashi, H., Sato, R., Maekawa, K. and Nakamura, H., eds., *Creep, Shrinkage and Durability Mechanic of Concrete and Concrete Sctructure,* London, UK: Taylor & Francis Group.

Bennett, M. and Doyle, P. (1997) *Environmental geology : geology and the human environment,* Chichester ; New York: J. Wiley.

Bentz, D. P., Geiker, M. R. and Hensen, K. K. (2001) 'Shrinkage-reducing admixtures and early-age desiccation in cement pastes and mortars', *Cement and Concrete Research,* 31(7).

Berge, B. (2000) *Ecology of Building Materials,* London, UK: Reed Educational and Professional Publishing Limited.

Bergoin, P. (1998) 'Lime After Vicat - Considerations', in Spano, U., ed. *Building Lime Forum 1998 Gathering,* Newry, Northern Ireland,

Bertos, M. F., Simons, S. J. R., Hills, D. C. and Carey, P. J. (2004) 'A review of accelerated carbonation technology in the treatment ofcement-based materials and sequestration of CO_2', *Journal of Hazardous Waste,* 112, 193-205.

Beruto, D. T. and Botter, R. (2000) 'Liquid-like H_2O adsorption layer to catalyze the $Ca(OH)_2/CO_2$ gas-solid reaction to form a non protective solid product layer at 20C', *Journal of the European Ceramic Society,* 20(4), 497-503.

Bindell, J. B. (1992) *Scanning Electron Microscopy, Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films,* Massachusetts, USA: Butterworth-Heinemann.

Binici, H., Shah, T., Aksogan, O. and Kaplan, H. (2008) 'Durability of concrete made with granite and marble as recycle aggregates', *Journal of Materials and Processing Technology,* 208(1-3), 299-308.

Blackburn, W. H. and Dennen, W. H. (1994) *Principles of Mineralogy,* 2nd ed., Iowa, USA: Wm C. Brown Publishers.

Blezard, R. G. (1998) 'The History of Calcareous Cement' in Hewlett, P., ed. *LEA's Chemistry of Cement and Concrete,* 4th ed., Massachusetts, USA: Elsevier Limited.

Bloodworth, A., Highley, D., Bate, R., Cameron, D., Lusty, P. and Rayner, D. (2009) *Silica Sand,* Nottingham, UK: British Geological Survey.

Bonewitz, R. L. (2012) *Rocks and Minerals,* London, UK: Dorling Kindersley Limited.

Borges, C., Santos Silva, A. and Veiga, R. (2013) 'Roles of aggregates in durability of air lime mortars: Influence of curing conditions', in Hughes, J. J., ed. *3rd Historic Mortar Conference,* Glasgow, Scotland, University of the West of Scotland,

Bouasker, M., Mounang, P., Turcry, P., Loukili, A. and Khelidj, A. (2008) 'Chemical shrinkage of cement pastes and mortars at very early age: Effect of limestone filler and granular inclusions', *Cement and Concrete Composites,* 30(1), 13-22.

Boynton, R. S. (1980) *Chemistry and technology of lime and limestone, Wiley-Interscience publication,* 2nd ed., New York ; Chichester: Wiley.

Bradley, I. (2002) *Chemistry,* Portsmouth, UK: Heinemann.

Brantley, L. R. and Brantley, R. T. (1996) *Building materials technology : structural performance and environmental impact,* New York ; London: McGraw-Hill.

Brezonik, P. and Arnold, W. (2011) *Water Chemistry: An Introduction to the Chemistry of Natural and Engineered Aquatic Systems,* New York, USA: Oxford University Press Inc.

Bridge, J. P. (1992) *Tile Your World: John Bridge's New Tile Setting Book,* Texas, USA: McGraw-Hill.

Bridgwood, B. and Lennie, L. (2013) *History, Performance and Conservation,* 2nd ed., Oxford, UK: Taylor & Francis.

British Standards, I. (2002) *BS EN 13139:2002 Aggregates for Mortar, British Standard,* London, UK: BSI.

Bui, D. D., Hui, J. and Stroeven, P. (2005) 'Particle size effect on the strength of the rice husk ash blended gap-graded Portland cement concrete', *Cement and Concrete Composites,* 27(3), 357-366.

Burek, C. and Stilwell, N. (2007) *Geodiversity Trail: Walking Through the Past on the University's Chester Campus,* Chester, UK: University of Chester.

Bushlaibi, A. H. and Alshamsi, M. A. (2002) 'Efficiency of curing on partially exposed high-strength concrete in hot climate', *Cement and Concrete Research,* 32(6), 949-953.

Cairncross, B. (2004) *Field Guide to Rocks & Minerals of Southern Africa,* South Africa: Struik Publishers.

Callister, W. D. (2010) *Materials Science and Engineering,* New York, USA: John Wiley & Sons.

Carino, N. J. (1994) 'The Maturity Method: Theory and Application', *Cement and Concrete,* 6(2).

Carran, D., Hughes, J., Leslie, A. and Kennedy, C. (2012) 'A Short History of the Use of Lime as a Building Material Beyond Europe and North America', *International Journal of Architectural Heritage: Conservation, Analysis and Restoration,* 6(2), 117-146.

Castro-Lacouture, D., A. Sefair, J., Flórez, L. and Medaglia, A. L. (2009) 'Optimization model for the selection of materials using a LEED-based green building rating system in Colombia', *Building and Environment,* 44.

Cebeci, O. Z., Ai-Noury, S. I. and Mirza, W. H. (1989) 'Strength and drying shrinkage of masonary mortars in various temperature-humidity environments', *Cement and Concrete Research,* 19.

Chamley, H. (2003) *Geosciences, Environment, and Man, Developments in earth & environmental sciences, 11571-9197,* Boston: Elsevier.

Chan, Y. N., Peng, G. F. and Anson, M. (1999) 'Residual strength and pore structure of high-strength concrete and normal strength concrete after exposure to high temperatures', *Cement and Concrete Composites,* 21(1), 23-27.

Chandra, S. (2003) *History of architecture and ancient building materials in India, part I & II,* New Delhi: Tech Books International.

Chang, L. L. Y., Howie, R., A. and Zussman, J. (1998) *Non-silicates: Sulphates, Carbonates, Phosphates, Halides,* 2nd ed., London: The Geological Society.

Chang, L. L. Y., Howie, R. A. and Zussman, J. J. (1996) *Sulphates, Carbonates, Phosphates and Halides, Rock-forming Minerals,* 2nd ed., Bath, UK: The Geological Society.

Charola, A. E. and Henriques, F. M. A. (1999) 'Hyraulicity In Lime Mortar Revisited' in Bartos, P., Groot, C. and Hughes, J. J., eds., *Proceedings PRO012: International RILEM Workshop on Historic Mortars: Characteristics and Tests Paisley, Scotland,* Edinburgh, Scotland: RILEM, 10.

Checova, E. (2009) *The Effect of Linseed Oil On The Properties Of Lime-Based Restoration Mortars,* unpublished thesis University of Bologna.

Cheng, V., Nga, E. and Givoni, B. (2005) 'Effect of envelope colour and thermal mass on indoor temperatures in hot humid climate', *Solar Energy,* 78(4), 528-534.

Cheung, J., Jeknavorian, A., Roberts, L. and Silva, D. (2011) 'Impact of admixtures on the hydration kinetics of Portland cement', *Cement and Concrete Research,* 41(12), 1289-1309.

Choi, C. S. and Kim, Y. W. (2000) 'A study of the correlation between organic matrices and nanocomposite materials in oyster shells formation', *Biomaterials,* 21(3), 213-222.

Civan, F. (2000) *Reservoir Formation Damage: Fundamentals, Modeling, Assessment, and Mitigation,* Texas, USA: Gulf Publishing Company.

Cizer, O., Van Balen, K. and Van Gemert, D. (2008) *Blended lime-cement mortars for conservation purposes: Microstructure and strength development Structural Analysis and Historic Construction,* London, UK: Taylor & Francis Group.

Cizer, O., Van Balen, K., Van Gemert, D. and Elsen, J. (2007) *Carbonation and hydrations of mortars with calcium hydroxide and calcium silicates binders,* translated by Coventry, UK: Taylor & Francis Group, 611-621.

Cobb, F. (2009) *Structural Engineer's Pocket Book,* 2nd. ed., Massachusetts, USA: Butterworth-Heinemann.

Cocks, F. H. (2009) *Energy Demand and Climate Change: Issues and Resolutions,* Durham, NC USA: Wiley-VCH. Copyright.

Corcione, C. E. and Frigione, M. (2011) 'UV-cured siloxane-modified acrylic coatings containing birifrangent calcarenitic stone particles: Photo-calorimetric analysis and surface properties', *Progress in Organic Coatings,* 72(3), 522-527.

Corinaldesi, V., Moriconi, G. and Naik, T. R. (2010) 'Characterization of marble powder for its use in mortar and concrete', *Ecological Engineering,* 24(1), 113-117.

Cowper, A. D., Building Research, S. and Building Research, E. (1998) *Lime and lime mortars,* Shaftesbury: Donhead.

Crishna, N., Banfill, P. F. G. and Goodsir, S. (2011) 'Embodied Energy and CO_2 in UK Dimension Stone', *Resources, Conservation and Recycling,* 55(12), 1265-1273.

Crow, J. M. (2008) *The Concrete Conundrum, Chemistry World,* London, UK: Royal Society of Chemistry.

Cruz-Romero, M., Kelly, A. L. and Kerry, J. P. (2007) 'Effects of high-pressure and heat treatments on physical and biochemical characteristics of oysters (Crassostrea gigas)', *Innovative Food Science & Emerging Technology,* 8(1), 30-38.

Cultrone, G., Sebastian, E. and Ortega Huertas, M. (2005) 'Forced and natural carbonation with and without additives: Mineralogy and textural changes', *Cement and Concrete Research,* 35, 2278-2289.

Damone, P. (2010) 'Concrete' in Damone, P. and Illston, J., eds., *Construction Materials: Their Nature and Behaviour*, 4th ed., Oxon, UK: Spon Press.

Dane, J. H. and Topp, G. C. (2002) *Methods of soil analysis: Physical Methods,* Washington DC, USA: Soil Science Society of America.

De Leeuw, N. H. and Parker, S. C. (1998) 'Surface Structure and Morphology of Calcium Carbonate Polymorphs Calcite, Aragonite and Veterite: An Optimistic Approach', *Journal of Physical Chemistry,* 102(16), 2914-2922.

De Oliveira, L. A. P., Gomes, J. P. C. and Pereira, C. N. G. (2006) 'Study of Sorptivity of Self-Compacting Concrete with Mineral Additions', *Journal of Civil Engineering and Management*, 12(3), 215-220.

Deb, P. S., Nath, P. and Sarker, P. K. (2013) 'Strength and permeation properties of slag blended fly ash based geopolymer concrete ', *Advanced Materials Research,* 651(1), 168-173.

Department of Environment, U. K. (1980) *Building in Hot Climate: A Selection of Overseas Building Notes*, London: Department of Environment.

Derr, H. M. (2012) *A Method of Petrographic Analysis, Based Upon Chromatic Interference with Thin Sections of Doubly-Refracting Crystals in Parallel Polarized Light,* South Carolina, USA: Nabu Press.

Desai, S. N., Patel, S. and Patil, H. H. (2011) 'Elevated Temperature Curing of Concrete with Industrial Wastes', *International Journal of Advanced Engineering Technology,* 2(4).

Dheilly, R. M., Tudo, J., Sebai bi, Y. and Quéneudec, M. (2002) 'Influence of storage conditions on the carbonation of powdered $Ca(OH)_2$', *Construction and Building Materials,* 16.

Dias, W. P. S. (2000) 'Reduction Of Concrete Sorptivity With Age Through Carbonation', *Cement and Concrete Research,* 30(8).

Dick, J. S. and Annicelli, R. A. (2001) *Rubber Technology: Compounding and Testing for Performance,* Ohio, USA: Hanser Publishers.

Diebel, J. and Norda, J. (2013) 'Historical Weather for 2012 in Sepang, Malaysia', [online], available: [Accessed 18 January 2014 2014].

Diekamp, A., Stalder, R., Konzett, J. and Mirwatt, P. W. (2012) 'Lime Mortar with Natural Hydraulic Components: Characterisation of Reaction Rims with FTIR Imaging in ATR-Mode' in Valek, J., Hughes, J. J. and Groot, C. J. W. P., eds., *Historic Mortars Characterisation, Assessment and Repairs,* Netherlands: Springer.

Dimes, F. G. (2011) 'Sedimentary Rocks' in Ashurst, J. and Dimes, F. G., eds., *Conservation of Building and Decorative Stone,* New York, US: Routledge.

Dimoudi, A. (2001) 'Microclimate' in Santamouris, M. I. and Asimakopoulos, D. N., eds., *Passive Cooling of Buildings*, London, UK: James & James (Science Publishers) Ltd.

Dotter, K. R. (2010) 'Historic Lime Mortars: Potential of Local Climate on the Evolution of Binder Morphology and Compostion' in Smith, B. J., Robin, C. and Gomez-heras, M., eds., *Limestone in the Built Environment: Present-day Challenges for the Preservation of the Past*, Bath, UK: The Geological Society Publishing House.

Eby, G. N. (2004) *Principles of Environmental Geochemistry*, California, USA: Thomson Learning.

Egerton, R. F. (2005) *Physical Principles of Electron Microscopy: An Introduction to TEM, SEM and AEM*, New York, USA: Springer.

El-Dieb, A. S. (2009) 'Mechanical, durability and microstructural characteristics of ultra-high-strength self-compacting concrete incorporating steel fibers', *Materials & Design*, 30(10), 4286-4292.

El-Turki, A., Ball, R. J. and Allen, G. C. (2007) 'The influence of relative humidity on structural and chemical changes during carbonation of hydraulic lime', *Cement and Concrete Research*, 37(8).

Elert, K., Rodriguez-Navarro, C., Pardo, E. S., Hansen, E. and Cazalla, O. (2002) 'Lime Mortars for the Conservation of Historic Buildings', *Studies in Conservation*, 47(1), 62-75.

Elizabeth, L. and Adams, C. (2005) *Alternative construction : contemporary natural building methods*, Hoboken, N.J.: John Wiley.

Ellis, L. (2006) 'Ceramics' in *Archaeology in Practise: A Student Guide to Archaeological Analyses*, Victoria, Australia: Blackwell Publishing.

Ellis, P. (2001) *Gauging Lime Mortar, The Building Conservation Directory 2001*, Wiltshire, United Kingdom: Cathedral Communications Limited.

Elsen, J. (2006) 'Microscopy of historic mortars—a review', *Cement and Concrete Research*, 36(8), 1416-1424.

Emmitt, S. and Gorse, C. A. (2006) *Barry's Advanced Construction of Buildings*, Oxford, UK: Blackwell Publishing Ltd.

Evangelista, L. and de Brito, J. (2010) 'Durability performance of concrete made with fine recycled concrete aggregates', *Cement and Concrete Composites*, 32(1), 9-14.

Ezziane, K., Bougara, A., Kadri, A., Khelafi, A. and Kadri, E. (2007) 'Compressive strength of mortar containing natural pozzolan under various curing temperature', *Cement and Concrete Composites*, 29(8), 587-593.

Faria, P. and Silva, V. (2013) 'Natural hydraulic lime mortar: influence of aggregates', in Hughes, J. J., ed. *3rd Historic Mortars Conference*, Glasgow, Scotland, University of the West of Scotland,

Farrar, D. and Hawe, M. (1985) 'Calcium Carbonate Dispersions', *United States Patent*, 4509987(442343),

Felice, M. (2013) *Material of the Month: Concrete, Materials World Magazine*, London, UK: The Institute of materials, Minerals and Mining.

Fennell, P. S., Davidson, J. F., Dennis, J. S. and Hayhurst, A. N. (2007) 'Regeneration of sintered limestone sorbents for the sequestration ofCO_2 from combustion and other systems', *Journal of the Energy Institute,* 80(2), 116-119.

Filippidis, A. and Georgakopoulos, A. (1992) 'Mineralogy and chemical investigation from fly ash from the Main and Northern lignite fields in Plotemais, Greece', *Fuel,* 71(4), 373-376.

Forsberg, A. and von Malmborg, F. (2004) 'Tools for environmental assessment of the built environment', *Building and Environment,* 39(2), 223-228.

Forster, A. M. (2002) *An assessment of the relationship between the water vapour permeability and hydraulicity of lime based mortars with particular reference to building conservation materials science,* unpublished thesis Heriot-Watt University.

Forster, A. M. (2004a) 'Hot Lime Mortar: A Current Perspective', *Journal of Architectural Conservation,* 3(10), 7-27.

Forster, A. M. (2004b) *How Hydraulic Lime Binders Work: Hydraulicity for Beginners and the Hydraulic Lime Family,* Edinburgh: Love Your Building Publishing.

Forster, A. M. (2004c) 'The Scottish Experience of Lime Mortar, Renders and Harlings', *International Journal for Restoration,* 10(6), 637-647.

Forster, A. M. (2007) 'Binder Loss In Traditional Mass Masonry: A Cause For Concern?', *Structural Survey,* 25(2), 148-170.

Forster, A. M. (2010a) 'Building conservation philosophy for masonry repair: Part 1 "Ethics"', *Structural Survey: Journal for Building Pathology & Refurbishment,* 28(2), 91-107.

Forster, A. M. (2010b) 'Building conservation philosophy for masonry repair: Part 2 "Principles"', *Structural Survey: Journal for Building Pathology & Refurbishment,* 28(3), 165-188.

Forster, A. M. and Carter, K. (2011) 'A framework for specifying natural hydraulic lime mortars for masonry construction', *Structural Survey,* 29(5), 373-396.

Forster, A. M., Carter, K., Banfill, P. F. G. and Kayan, B. (2011) 'Green Maintenance for Historic Masonry Buildings: An Emerging Concept', *Building Research and Information,* 39(6), 656-664.

Forster, A. M. and Douglas, J. E. (2010) 'Condition Survey Objectivity & Philosophy Driven Masonry Repair: An Increased Probability For Project Divergence?', *Structural Survey: Journal for Building Pathology & Refurbishment,* 28(5), 384-407.

Forster, A. M., Razali, N., Banfill, P. F. G., Szadurski, E. and Torney, C. (2013) 'The influence of calcitic filler in hydraulic lime mortars for use in high temperature & high humidity climatic conditions: A preliminary investigation', in Hughes, J. J., ed. *3rd Historic Mortar Conference,* Glasgow, Scotland, University of the Western of Scotland,

Forster, A. M. and Szadurski, E. M. (2012) *Binder Leaching of Naturally Hydraulic Lime (NHL) Mortars,* translated by RICS, Las Vegas, USA: RICS, 671-678.

Forsyth, M. (2007) *Understanding historic building conservation, Historic building conservation.,* Oxford: Blackwell Publishing.

Fox, M. A. and Whitesell, J. K. (2003) *Organic Chemistry and Biochemistry,* Sudbury, USA: Jones & Bartlett Publishers.

French, H. M. (2007) *The Periglacial Environment,* 3rd. ed., West Sussex, England: John Wiley & Sons.

Frew, C. (2007) *Pointing With Lime: The Building Conservation Directory,* Tisbury: Cathedral Communications Limited.

Garber, G. (2006) *Design and Construction of Concrete Floors,* 2nd ed., Massachusetts, USA: Butterworth-Heinmann.

Garcia, E. J. I. and Sharp, J. H. (1998) 'Effects of Temperature on Hydration of Main Clinkers Phases in Portland Cements: Part 1', *Cement and Concrete Research,* 28(9)(9), 1259-1274.

GB (2007) *Waste Strategy For England 2007*, London: Stationery Office.

Gebrehiwet, T. A., Redden, G. D., Fujita, Y., Beig, M. S. and Smith, R. W. (2012) 'The Effect of the $CO_3{}^{2-}$ to Ca^{2+} Ion activity ratio on calcite precipitation kinetics and Sr^{2+} partitioning', *Geochemical Transactions,* 13(1), 1-11.

Genestar, C. and Pons, C. (2003) 'Ancient covering plaster mortars from several convents and Islamic and Gothic palaces in Palma de Mallorca (Spain): Analytical characterisation', *Journal of Cultural Heritage,* 4(4), 291-298.

Georgali, B. and Tsakiridis, P. E. (2005) 'Microstructure of fire-damaged concrete: A case study', *Cement and Concrete Composite,* 27(2), 255-259.

George, K., Ziska, L. H., Bunce, J. A. and Quebedeaux, B. (2007) 'Elevated atmospheric CO_2 concentration and temperature across an urban–rural transect ', *Atmospheric Environment,* 41(35), 7654-7665.

Gesoglu, M. (2010) 'Influence of steam curing on the properties of concretes incorporating metakaolin and silica fume', *Materials and Structures,* 43(8).

Ghosh-Dastidar, A., Mahuli, S. K., Agnihotri, R. and Liang, S. F. (1996) 'Investigation of High-Reactivity Calcium Carbonate Sorbent for Enhanced SO2 Capture', *Industrial & Chemical Engineering Research,* 35(2), 598-606.

Gibbons, P. and Newsom, S. (2003) *Preparation and Use of Lime Mortars, Technical Advice Note,* Edinburgh, Scotland: Historic Scotland.

Gibbons, P., Newsom, S., Scotland, H. and Technical Conservation, R. a. E. D. (2003) *Preparation and use of lime mortar, Historic Scotland technical advice note,* Rev. ed., Edinburgh: Historical Scotland.

Givoni, B. (1998) *Climate Considerations in Building and Urban Design,* NY, USA: John Wiley & Sons.

Gleize, P. J. P., Muller, A. and Roman, H. R. (2003) 'Micro-structural Investigation of a Silica Fume-Cement-Lime Mortar', *Cement and Concrete Composites,* 25(2), 171-175.

Gonen, T. and Yazicioglu, S. (2007) 'The influence of compaction pores on sorptivity and carbonation of concrete', *Construction and Building Materials,* 21(5), 1040-1045.

Gopalakrishnan, K., Birgisson, B., Taylor, P. C. and Attoh-Okine, N. O. (2011) 'Introduction' in Gopalakrishnan, K., Birgisson, B., Taylor, P. C. and Attoh-Okine, N. O., eds., *Nanotechnology in Civil Engineering,* Berlin, Germany: Springer- Verlag.

Gourdin, W. H. and Kingery, W. D. (1975) 'The Beginning of Pyrotechnology: Neolithic and Egyptian Lime Plaster', *Journal of Field Archaeology,* 2, 133-150.

Graedel, T. E. (1999) 'Environmentally Superior Buildings from Birth to Death' in Kibert, C. J., ed. *Reshaping the Built Environment: Ecology, Ethics and Economics*, Washington DC, USA: Island Press.

Graham, P. (2003) *Building Ecology: First Principles For A Sustainable Built Environment,* Oxford, UK: Blackwell Science Ltd.

Gray, M., Goldfine, A., Rosenthal, L. and Carnahan, L. (2010) 'Conformance Testing',

Groot, C. and Larbi, J. (1999) 'The Influence of Water Flow (Reversal) on Bond Strength Development in Young Masonry', 44(2).

Gueguen, Y. and Palciauskas, V. (1994) *Introduction to the Physics of Rocks,* New Jersey, US: Princeton University Press.

Guemmadi, Z., Resheidat, M., Chabil, H. and Toumi, B. (2009) 'Modelling the Influence of Limestone Filler on Concrete: A Novel Approach for Strength and Cost ', *Jordan Journal of Civil Engineering,* 3(2), 158-171.

Guinier, A. (1994) *X-ray Diffraction in Crystal, Imperfect Crystal and Amorphous Body,* New York, USA: Dover Publications.

Hadj-sadok, A., Kenai, S., Courardc, L. and Darimon, A. (2011) 'Microstructure and durability of mortars modified with medium active blast furnace slag', *Construction and Building Materials,* 25(2), 1018-1025.

Hageman, J. M. (2008) *Contractor's Guide to the Building Code,* California, USA: Craftsman Book Company.

Haggett, P. (2002) *Encyclopedia of World Geography: Southeast Asia,* Oxfordshire, UK: Andromeda Oxford Ltd.

Hall, C., Hamilton, A., Hoff, W. D., Viles, H. A. and Eklund, J. A. (2010) 'Moisture dynamics in walls: response to micro-environment and climate change', *Royal Society A: Mathematical, Physical & Engineering Sciences,* 467(2125).

Hall, C. and Hoff, W. D. (2002) *Water Transport in Brick, Stone and Concrete,* London: Taylor & Francis.

Hall, C. and Hoff, W. D. (2012) *Water Transport In Brick, Stone And Concrete,* Oxon, UK: Spon Press.

Hall, C., Hoff, W. D., Taylor, S. C., Wilson, M. A., Yoon, B. G., Reinhardt, H. W., Sosoro, M., Meredith, P. and Donald, A. M. (1995) 'Water anomaly in capillary liquid absorption by cement-based materials', *Journal of Materials Science Letters,* 14(17), 1178-1181.

Hammond, G. P. and Jones, C. I. (2008) 'Embodied energy and carbon in construction materials', *Proceedings of Institution of Civil Engineers: Energy,* 161(2), 87-98.

Hanley, R. and Pavia, S. (2008) 'A study of workability of natural hydraulic lime mortars and its influence on strength', *Materials and Structures,* 41(2), 373-381.

Hanžic, L. and Ilić, R. (2003) 'Relationship between liquid sorptivity and capillarity in concrete', *Cement and Concrete Research,* 33(9).

Hassibi, M. (1999) *An Overview of Lime Slaking and Factors That Affect The Process,* translated by New Orleans, USA.

Hauser, B. (2002) *Drinking Water Manual: A Laboratory Manual,* Florida, USA: Lewis Publishers.

Hawkins, P., Tennis, P. and Detwiler, R. (2003) 'The USe of Limestone in Portland Cement: A State of the Art Review', 44.

Healy, J. F. (1999) *Pliny the Elder on Science and Technology,* Oxford, UK: Oxford University Press.

Hewlett, P. (2004) *Lea's Chemistry of Cement and Concrete,* 4th ed., Butterworth-Heinemann.

Holmes, S. and Wingate, M. (2002) *Building with lime : a practical introduction,* Rev. ed., London: ITDG.

Hopkins, B. L. (2008) *Terrapin Run: A Mockery of "AD HOCKERY',* unpublished thesis Morgan State University.

Hsiao, C. M. and Zhang, Y. M. (2000) *Iron and Steels, Microstructure and Properties of Materials,* Singapore: World Scientific Publishing Co.

Huang, B., Wu, H., Shu, X. and Burdette, E. G. (2010) 'Laboratory evaluation of permeability and strength of polymer-modified pervious concrete', *Construction and Building Materials,* 24(5), 818-823.

Hughes, D., Swann, S. and Gardner, A. (2007) 'Roman Cement Part One: Its Origin and Properties', *Journal of Architecture and Conservation,* 13(1), 21-36.

Hughes, J. J. and Cuthbert, S. J. (2000) 'The petrography and microstructure of medieval lime mortars from the west of Scotland: Implications for the formulation of repair and replacement mortars', *Materials and Structures,* 33(9), 594-600.

Hughes, J. J. and Valek, J. (2003) *Mortars in Historic Building: A Review of the Conservation, Technical and Scientific Literature, Technical Advice Notes,* Edinburgh, Scotland: Historic Scotland.

Hughes, J. J., Válek, J. and Historic Scotland. Technical Conservation, R. a. E. D. (2003) *Mortars in historic buildings : a review of the conservation, technical and scientific literature, Literature review,* Edinburgh: Historic Scotland.

Hughes, P. (1986) 'The Need For Old Buildings To "Breathe"',

Hyde, R. (2000) *Climate Responsive Design,* London, UK: E & FN Spon.

Hyde, R. and Rostvik, N. (2008) 'Definitions, Concepts and Principles' in Hyde, R., ed. *Bioclimatic Housing: Innovative Design for Warm Climate*, London, UK: Earthscan.

Hyslop, E. K., Albornoz-Parra, L., Maxwell, I., McMillan, A. A., Walsh, J., British Geological, S., International Association of Engineering, G., Natural Environment Research, C. and

Unesco (2006) *Stone in Scotland, Earth science series (Houston, Tex.),* Paris: UNESCO.

Illston, J. M., Domone, P. L. J. and NetLibrary, I. (2001) *Construction materials : their nature and behaviour,* 3rd ed., London: Spon.

IMF (2013) 'World Cement Production in 2012', *World Economic Outlook 2013*, Washington DC, USA: IMF,

Ingram, J. P. (2009) 'Application of petrographic examination techniques to the assessment of fire-damaged concrete and masonry structures', *Materials Characterization,* 60(7), 700-709.

Ishida, T. (2009) 'Life-span Simulation of Reinforced Concrete Structures: Towards Rational Stock Management' in Fujino, Y. and Noguchi, T., eds., *Stock Management for Sustainable Renegeration*, Tokyo, Japan: Springer.

Izaguirre, A., Lanas, J. and Álvarez, J. I. (2009) 'Effect of water-repellent admixtures on the behaviour of aerial lime-based mortars', *Cement and Concrete Research,* 39(11), 1095-1104.

Jackson, N. and Dhir, R. K. (1996) *Civil Engineering Materials,* 5th ed., London, UK: Macmillan Press LTD.

Jegatheesan, V., Liow, J. L., Shu, L., Kim, S. H. and Visvanathan, C. (2009) 'The need for global coordination in sustainable development', *Journal of Cleaner Production,* 17(7), 637-643.

Jianga, L., Lin, B. and Cai, Y. (2000) 'A model for predicting carbonation of high-volume fly ash concrete', *Cement and Concrete Research,* 30(5), 699-702.

Kalagri, A., Karatasios, I. and Kilikoglou, V. (2014) 'The effect of aggregate size and type of binder on microstructure and mechanical properties of NHL mortars', *Construction and Building Materials,* 53, 467-474.

Kanna, V., Olson, R. A. and Jennings, H. M. (1998) 'Effect of shrinkage and moisture content on the physical characteristics of blended cement mortars', *Cement and Concrete Research,* 28 (10)(10), 1467-1477.

Karakaş, F. and Çelik, M. S. (2012) 'Effect of quantity and size distribution of calcite filler on the quality of water borne paints', *Progress in Organic Coatings,* 74(3), 555-563.

Kavas, T. and Olgun, A. (2007) 'Properties of Cement and Mortar Incorporating Marble Dust and Crushed Bricks', *Ceramics,* 52(1), 24-28.

Kerr, E. A. (2008) *Damage Mechanism and Repairability of High Strength Concrete Exposed to Heat*, unpublished thesis University of Notre Dame.

Khatib, J. M. and Mangat, P. S. (1995) 'Absorption characteristics of concrete as a function of location relative to casting position', *Cement and Concrete Research,* 25(5).

Kibert, C. J. (1999) 'The Promises and Limits of Sustainability' in Kibert, C. J., ed. *Reshaping the Built Environment: Ecology, Ethics and Economics,* Washington DC, USA: Island Press.

Kibert, C. J. (2008) *Sustainable Construction: Green Building Design and Delivery* New Jersey, USA: John Wiley & Sons Inc.

Kidwell, D. M. (2007) *Habitat use of surf scoters wintering in the mesohaline region of the mainstem Chesapeake Bay, Maryland*, unpublished thesis University of Maryland.

Kim, J. K., Moon, Y. H. and Eo, S. H. (1998) 'Compressive strength development of concrete with different curing time and temperature', *Cement and Concrete Research*, 28(12), 1761-1773.

King, H. (2005) 'The 'Acid Test' for Carbonate Minerals and Carbonate Rocks', [online], available: [Accessed 19 January 2014 2014].

Kingery, W. D., Prickett, M. and Vandiver, P. B. (1988) *The beginnings of pyrotechnology - II: Production and use of lime and gypsum plaster in the pre-pottery Neolithic Near East.*

Kogel, J. E. (2006) *Industrial minerals & rocks : commodities, markets, and uses*, 7th ed., Littleton, Colo.: Society for Mining, Metallurgy and Exploration

Korjakins, A., Shakhmenko, G., Bajare, D. and Bumanis, G. (2012) 'Effect of Ground Glass Fineness on Physical and Mechanical Properties of Concrete', in *10th International Congress for Applied Mineralogy (ICAM)*, Norway, Springer Berlin Heidelberg,

Kotz, J., Treichel, P. and Townsend, J. (2009) *Chemistry and Chemical Reactivity*, 7th ed., Stamford, USA: Cengage Learning Inc.

Kubota, T., Chyee, D. T. H. and Ahmad, S. (2009) 'The effects of night ventilation technique on indoor thermal environment for residential buildings in hot-humid climate of Malaysia', *Energy and Buildings*, 41(8), 829-839.

Lam, K. and Morton, B. (2004) 'The Oysters of Hong Kong (Bivalvia: Ostreidae And Gryphaeidae)', *The Raffles Bulletin of Zoology*, 52(1), 11-28.

Lanas, J. and Alvarez-Galindo, J. I. (2006) 'Masonry repair lime-based mortar: factors affecting the mechanical behaviours', *Cement and Concrete Research*, 33(11), 1867-1878.

Lanas, J., Pérez Bernal, J. L., Bello, M. A. and Alvarez, J. I. (2006a) 'Mechanical properties of masonry repair dolomitic lime-based mortars', *Cement and Concrete Reseach*, 36(5).

Lanas, J., Sirera, R. and Alvarez, J. I. (2005) 'Compositional changes in lime-based mortars exposed to different environments', *Thermochimica Acta*, 429(2), 219-226.

Lanas, J., Sirera, R. and Alvarez, J. I. (2006b) 'Study of the mechanical behaviour of masonry repair lime-based mortars cured and exposed under different conditions', *Cement and Concrete Research*, 36(5).

Lange, L. C., Hills, C. D. and Poole, A. B. (1996) 'The influence of mixed parameters and binder choice on the carbonation of cement solidified wastes', *Waste Management*, 16(8), 665-773.

Lawrence, R. M., Timothy, J. M., Rigby, S. P., Walker, P. and D'Ayala, D. (2007) 'Effects of carbonation on the pore structure of non-hydraulic lime mortars', *Cement and Concrete Research*, 37(7), 10.

Lawrence, R. M. H. (2006) *A study of carbonation in non-hydraulic lime mortars*, unpublished thesis University of Bath.

Le Quere, C. (2013) *Global Carbon Budget*, Earth Syst. Sci. Data Discussion

Lee, C. H., Lee, D. K., Ali, M. A. and Kim, P. J. (2008) 'Effects of oyster shell on soil chemical and biological properties and cabbage productivity as a liming materials', *Waste Management,* 28(12), 2702-2708.

Lee, C. Y., Lee, H. K. and Lee, K. M. (2003) 'Strength and microstructural characteristics of chemically activated fly ash–cement systems', *Cement and Concrete Research,* 33(3), 425-431.

Lee, S. W., Jang, Y. N. and Kim, J. C. (2011) 'Characteristics of the Aragonitic Layer in Adult Oyster Shells, *Crassostrea gigas*: Structural Study of Myostracum including the Adductor Muscle Scar', *Evidence Based Complementary and Alternative Medicine,* 2011(1), 1-10.

Leslie, A. and Gibbons, P. (2005) *Technical Advice Notes 19: Scottish Aggregate For Building Conservation,* Edinburgh: Historic Scotland.

Lewin, S. Z. (1981) 'X-ray diffraction and scanning electron microscope analysis of conventional mortars ', in ICCROM, ed. *Mortars, Cements and Grouts Used In the Conservation of Historic Building: Symposium,* Rome, ICCROM, 101-131.

Li, B., Wang, J. and Zhou, M. (2009) 'Effect of limestone fines content in manufactured sand on durability of low- and high-strength concretes', *Construction and Building Materials,* 23(8), 2846-2850.

Li, Y. Y. (2004) 'China's way forward paved in cement', *Asia Times,* **7 January 2004**,

Lian, C. and Zunge, Y. (2010) 'Optimum mix design of enhanced permeable concrete – An experimental investigation', *Construction and Building Materials,* 24(12), 2664-2671.

Liang, C. F. and Wang, H. Y. (2013) 'Feasibility of Pulverized Oyster Shell as a Cementing Material', *Advances in Materials Science and Engineering,* 2013(1), 7.

Lindqvist, J. E. and Sandstrom, M. (2000) 'Quantitative analysis of historical mortars using optical microscopy', *Materials and Structure,* 33(10), 612-617.

Liu, C. (2000) 'Study of the Traditional Method of Lime Slaking and Lime Products Making in Beijing, China' in Bartos, P., Groot, C. and Hughes, J. J., eds., *Historic Mortars: Characteristics and Tests*, France: RILEM.

Liu, Y. X., Yang, T. O., Yuan, D. X. and Wu , X. Y. (2010) 'Study of municipal wastewater treatment with oyster shell as biological aerated filter medium', *Desalination,* 254(1-3), 149-153.

Lo, Y. and Lee, H. M. (2002) 'Curing effects on carbonation of concrete using a phenolphthalein indicator and Fourier-transform infra-red spectroscopy', *Building and Environment,* 37(5).

Lottermoser, B. G. (2010) *Mine Wastes: Characterization, Treatment and Environmental Impacts,* Berlin: Springer-Verlag.

Lowe, E. A. (1999) 'Sustainable New Towns and Industrial Ecology' in Kibert, C. J., ed. *Reshaping the Built Environment: Ecology, Ethics and Economics*, Washington DC, USA: Island Press.

Lucas, A. (2008) *Ancient Egyptian materials & industries, Kessinger Publishing's rare reprints,* 3rd. , rev. ed., [Whitefish, Mont.]: Kessinger Publishing Co.

Lutz, M. P., Monteiro, P. J. M. and Zimmerman, R. W. (1997) 'Inhomogeneous Interfacial Transition Zone Model For The Bulk Modulus Of Mortar', *Cement and Concrete Research*, 27(7), 1113-1122.

Lyons, A. (2010) *Materials for architects and builders*, 4th ed., Amsterdam ; London: Butterworth-Heinemann.

M., K. (2007) *Characterization of Precipitated Calcium Carbonate (PCC) compounds on the basis of powder X-ray diffraction data*, unpublished thesis Universitat Karlshruhe.

Mack, R. C. and Speweik, J. P. (1998) *Technical Preservation Services: Repointing Mortar Joints in Historic Masonry Buildings*, Washington, D.C.: US Department of Interior.

Mahasenan, N., Smith, S. and Humphreys, K. (2003) 'The Cement Industry and Global Climate Change: Current and Potential Future Cement Industry CO2 Emissions' in Gale, J. and Kaya, Y., eds., *Greenhouse Gas Control Technologies - 6th International Conference* [doi: DOI: 10.1016/B978-008044276-1/50157-4], Oxford: Pergamon, 995-1000.

Malhotra, V. M. (2006) 'Non-destructive Test' in Lamond, J. F. and Pielert, J. H., eds., *Significance of Test and Properties of Concrete & Concrete Making Materials*, Pennsylvania, USA: ASTM International.

Malin, N. (1999) 'Environmentally Responsible Building Materials Selection' in Kibert, C. J., ed. *Reshaping the Built Environment: Ecology, Ethics and Economics*, Washington DC, USA: Island Press.

Mallinson, L. G. and Davies, I. L. (1987) ' A historical examination of concrete', *Final Report CD-NA-10937-EN-C.*

Marques, S. F., Ferreira, V. M., Labrincha, V. M. and Silva, S. M. (2006) 'Study of Old and Rehabilitation by Common Analytical Techniques' in Fort, R., Alvarez de Buergo, M., Gomez-Heras, M. and Vasques-Caldo, C., eds., *Heritage, Weathering and Conservation*, London, UK: Taylor and Francis Group.

Martin, R. (2013) *Earth Evolving System: The History of Planet Earth,* Burlington, USA: Jones & Bartlett Learning.

Mason, K. and Hill, N. (1999) *The small-scale vertical shaft lime kiln : a practical guide to design, construction and operation,* London: Intermediate Technology.

Materic, V. and Smedley, S. I. (2011) 'High Temperature Carbonation of Ca(OH)2', *American Chemical Society,* 50(10), 5927-5932.

Maxwell, I. (1995) 'Introduction To Lime In Scotland', in Ward, J. D. and Maxwell, I., eds., *The Historic Scotland International Lime Conference*, The Building Limes ForumHistoric Scotland, 5-22.

Maxwell, I. (2008) *Stone in context : 14 and 15 November 2007, Tolbooth, Stirling, Conference proceedings (Historic Scotland. Technical Conservation Research and Education Group),* Edinburgh: Historic Scotland.

McElroy, M. B. (2002) *The Atmospheric Environment: Effects of Human Activity,* New Jersey, USA: Princeton University Press.

Mcmillan, A., Hyslop, E., Maxwell, I. and Mckinney, A. (2006) 'Indigenous Stone Resources for Scotland's Built Heritage', in *10th IAEG International Congress*, Nottingham, United Kingdom, The Geological Society of London, McMullen, C. P. and Jabbour, J. R. (2009) *Climate Change Science Compendium 2009,* Nairobi, Kenya: UNEP.

Meier, A., Bonaldi, E., Cella, G. M., Lipinski, W. and Wuillemin, D. (2006) 'Solar chemical reactor technology for industrial production of lime', *Solar Energy,* 80(10), 1355-1362.

Menezesa, R. R., Ferreira, H. S., Neves, G. A., Lira, H. D. L. and Ferreira, H. C. (2005) 'Use of granite sawing wastes in the production of ceramic bricks and tiles', *Journal of the European Ceramic Society,* 25(7), 1149-1158.

Middendorf, B., Hughes, J. J., Callebaut, K., Baronio, G. and Papayianni, I. (2005) 'Investigative methods for the characterisation of historic mortars—Part 1: Mineralogical characterisation', *Materials and Structures,* 38(8), 761-769.

Mihajlović, S., Sekulić, Z., Daković, A., Vučinić, D., Jovanović, V. and Stojanović, J. (2009) 'Surface properties of natural calcite filler Treated with stearic acid', *Ceramics - Silikaty,* 53(4), 268-275.

Miller, A. W., Reynolds, A. C., Sobrino, C. and Riedel, G. F. (2009) 'Shellfish Face Uncertain Future in High CO_2 World: Influence of Acidification on Oyster Larvae Calcification and Growth in Estuaries', *PLOS ONE,* 4(5), 1-8.

Mills, L., Burnstock, A., Duarte, F., de Groot, S., Megens, L., Bisschoff, M., Van Kuelen, H. and Van Der Berg, K. J. (2008) 'Water Sensitivity of Modern Artists' Oil Paints', in Brigland, J., ed. *15th Triennial Conference,* New Delhi, India, International Council of Museum,

Ming, D. W. (2006) 'Carbonates' in Lal, R., ed. *Encyclopedia of Soil Science,* 2nd ed., Florida, USA: Taylor & Francis Group.

Mitchell, D. S. (2007) *The Use of Lime & Cement in Traditional Buildings,* Edinburgh, Scotland: Historic Scotland.

Miyake, M., Komarneni, S. and Roy, R. (1988) 'Immobilization of Pb^{2+}, Cd^{2+}, Sr^{2+} and Ba^{2+} ions using calcite and aragonite', *Cement and Concrete Research,* 18(3), 485-490.

Modena, C., Loureno, P. B. and Roca, P. (2005) *Structural analysis of historical constructions : possibilities of numerical and experimental techniques,* 1st ed., Leiden ; London: A.A. Balkema Publishers.

Monroe, J. S. and Wicander, R. (2014) *The Changing Earth: Exploring Geology and Evolution,* 7th ed., California, USA: Cengage Learning Inc.

Moorehead, D. R. (1986) 'Cementation by the carbonation of hydrated lime', *Cement and Concrete Research,* 16(5), 700-708.

Moosberg-Bustnes, H., Lagerblad, B. and Forssberg, E. (2004) *Materials and Structures,* 37(2), 74-81.

Moropoulou, A., Bakolas, A. and Bisbikou, K. (2000) 'Investigation of the technology of historic mortars', *Journal of Cultural Heritage,* 1(1), 45-58.

Moropoulou, A., Bakolas, A., Moundoulas, P., Aggelakopoulou, E. and Anagnostopoulou , S. (2005) 'Strength development and lime reaction in mortars for repairing historic masonries', *Cement and Concrete Composites,* 27(2), 289-294.

Moropoulou, A., Bakolasb, A. and Bisbikou, K. (1995) 'Characterisation of ancient, Byzantine and later historic mortars by thermal and X-ray diffraction techniques', *Thermochimica Acta*, 269-270, 779-795.

Moropoulou, A., Biscontin, G., Bakolas, A. and Bisbikou, K. (1997) 'Technology and behaviour of rubble masonry mortars', *Construction Building Materials,* 11(2), 119-129.

Mostafa, N. Y. and Brown, P. W. (2005) 'Heat of hydration of high reactive pozzolans in blended cements', *Thermochimia Acta*, 435(2), 162-167.

Myers, R. L. (2007) *The 100 Most Important Chemical Compounds: A Reference Guide,* Connecticut, US: Greenwood Publishing Group.

Nadif, A., Hunkeler, D. and Kauper, P. (2002) 'Sulfur-free lignin from alkaline pulping tested in mortar for use in mortar additives', *Bioresource Technology,* 84(1), 49-55.

Natalio, F., Corrales, T. P., Panthöfer, M., Schollmeyer, D., Lieberwirth, I., Müller, W. E. G., Kappl, M., Butt, H. J. and Tremel, W. (2013) 'Flexible Minerals: Self-Assembled Calcite Spicules with Extreme Bending Strength', *Science,* 339(6125), 1298-1305.

Naus, D. J. (2005) *The Effects of Elevated Temperature on Concrete Materials and Structures: Literature Review,* Tennessee, USA: US Nuclear Regulatory Commission.

Nebel, H., Neumann, M., Mayer, C. and Epple, M. (2008) 'On the Structure of Amorphous Calcium Carbonate—A Detailed Study by Solid-State NMR Spectroscopy', *Inorganic Chemistry,* 47(17), 7874-7879.

Nesse, W. D. (2000) *Introduction To Mineralogy,* New York, USA: Oxford University Press, Inc.

Neville, A. M. (1996) *Properties of concrete,* 4th and final ed., New York: Wiley.

Neville, A. M. (2002) *Properties of Concrete,* 4th ed., Essex, UK: Pearson Education Limited.

Neville, A. M. and Brooks, J. J. (2010) *Concrete technology,* 2nd ed., Harlow, England ; New York: Prentice Hall.

Nichols, G. (2009) *Sedimentology and Stratigraphy,* 2nd ed., West Sussex, UK: Wiley-Blackwell.

Noguchi, T. and Nemati, K. M. (1995) 'Relationship between compressive strength and modulus of elasticity of High-Strength Concrete ', *Journal of Structural and Construction Engineering,* 474(1), 1-10.

NPCS, B. (2012a) *Details Project Profiles on Chemical Industries,* 2nd ed., New Delhi, India: NIIR Project Consultancy Services.

NPCS, B. (2012b) *Select & Start Your Own Industry,* New Delhi, India: NIIR Project Consultantcy Services.

Oates, J. A. H. (1998) *Lime and limestone : chemistry and technology, production and uses,* Weinheim ; Chichester: Wiley-VCH.

Odgers, D. and Henry, A. (2012) *Practical Building Conservation: Stone,* London, UK: English Heritage.

Odler, I. (2006) 'Hydration, Setting and Hardening of Portland Cement ' in Hewlett, P. C., ed. *Lea's Chemistry of Cement and Concrete,* Oxford, UK: Elsevier.

Odom, J. D. and Dubose, G. (2000) *Commissioning Buildings in Hot Humid Climates: Design & Construction Guidelines*, Georgia, USA: The Fairmont press Inc.

Ogino, T., Suzuki, T. and Sawada, K. (1987) 'The Formation and Transformation Mechanism of Calcium Carbonate in Water', *Geochimia et Cosmochimia Acta,* 51(10), 2757-2767.

Oliver, J. E. (2005) *Encyclopaedia of World Climatology,* The Netherlands: Springer.

Olivia, M. and Nikraz, H. R. (2011) 'Corrosion performance of the embedded steel in fly ash geopolymer concrete by impressed voltage method ' in Fragomeni, Venkatesan, Lam and Setunge, eds., *Incorporating Sustainable Practice in Mechanics of Structures and Materials*, London,UK: Taylor & Francis Group.

Ortiz, O., Castells, F. and Sonnemann, G. (2009) 'Sustainability in the construction industry: A review of recent developments based on LCA', *Construction and Building Materials,* 23(1), 28-39.

Osman, M. A., Atallah, A., Schweizer, T. and Ottinger, H. C. (2004a) 'Particle–particle and particle-matrix interactions in calcite filled high-density polyethylene—steady shear ', *Journal of Rheology,* 48(5), 1167-1184.

Osman, M. A., Atallah, A. and Suter, U. W. (2004b) 'Influence of excessive filler coating on the tensile properties of LDPE–calcium carbonate composites', *Polymer,* 45(4), 1177-1183.

Osman, M. A. and Suter, U. W. (2002) 'Surface treatment with calcite with fatty acids: structures and properties of the organic monolayer', *Chemistry of Materials,* 14(10), 4408-4415.

Othman, S. (2005) *A Numerical Study Of Transient Natural Convection Of Water Near Its Density Extremum*, unpublished thesis University of Strathclyde.

O'Farrell, M., Wild, S. and Sabir, B. B. (2001) 'Sorptivity and Water Absorption of Mortars Incorporating Waste Clay Brick', *American Concrete Institute,* 199(1), 853-868.

Pacheco Torgal, F., Miraldo, S., Labrincha, J. A. and De Brito, J. (2012) 'An overview on concrete carbonation in the context of eco-efficient construction: Evaluation, use of SCMs and/or RAC', *Construction and Building Materials,* 36.

Paulou, K. (2003) 'Pre-testing of Self Compacting Concrete with Various Mineral Additives and Admixture' in Wallevik, O. H. and Nielsson, I., eds., *Self Compacting Concrete*, France: RILEM.

Pavia, H. S. (2008) 'A study of the workability of natural hydraulic lime mortars and its influence on strength', *MATERIALS AND STRUCTURES,* 41(2).

Pavia, S. and Caro, S. (2008) 'An Investigation of Roman Mortar Technology Through the Petrograhic Analysis of Archaeological Material', *Construction and Building Materials,* 22(8), 1807-1811.

Pavia, S. and Hanley, R. (2009) 'Flexural bond strength of natural hydraulic lime mortar and clay brick', *Materials and Structures,* 43(7), 913-922.

Pentecost, A. (2005) *Travertine,* The Netherlands: Springer-Verlag Berlin Heidelberg.

Pera, J., Husson, S. and Guilhot, B. (1999) 'Influence of finely ground limestone on cement hydration', *Cement and Concrete Composites,* 21(2).

Perić, J., Vučak, M., Krstulović, R., Brečević, L. J. and Kralj, D. (1996) 'Phase transformation of calcium carbonate polymorphs', *Thermochimica Acta,* 277(1), 175-186.

Peters, J. B., Kelling, K. A. and Shultze, E. E. (1996) *Choosing Between Liming Materials,* Wisconsin, USA: University of Wisconsin-Extension.

Petersen, J. F., Sack, D. and Gabler, R. E. (2011) *Physical Geography,* 10th ed., California, USA: Brooks/Cole Cengage Learning.

Pitroda, J. and Umrigar, F. S. (2013) 'Evaluation of Sorptivity and Water Absorption of Concrete with Partial Replacement of Cement by Thermal Industry Waste (Fly Ash)', *International Journal of Engineering and Innovative Technology,* 2(7), 245-249.

Poigner, H., Nehrke, G., Brey, T., Abele, D. and Wilhelms-Dick, D. (2011) 'Coexistence of three calcium carbonate polymorphs in the shell of the Antarctic clam Laternula elliptica: Consequences for trace metal incorporation', in *European Geophysical Union General Assembly*, Vienna, Austria,

Polk, P. (2012) *Collecting Rocks, Gems and Minerals: Identification, Values and Lapidary Uses,* 2nd ed., Wisconsin, USA: Krause Publication.

Poon, C. S., Shui, Z. S. and Lam, L. (2004) 'Effect of microstructure of ITZ on compressive strength of concrete prepared with recycled aggregates', *Construction and Building Materials,* 18(6), 461-468.

Poyet, S. and Charles, S. (2009) 'Temperature dependence of the sorption isotherms of cement-based materials: Heat of sorption and Clausius–Clapeyron formula', *Cement and Concrete Research,* 31(11), 1060-1067.

Prabhakar, K., Pankaj, S., Pathak, R. P., Sameer, V., Mahure, N. V. and Ratnam, M. (2013) 'Concrete exposed to hot water springs - It's designing and monitoring post construction performance - A case study', *International Journal of Civil & Structural Engineering,* 4(2), 125-135.

Prezant, B., Weekes, D. M. and Miller, J. D. (2008) *Recognition, Evaluation, and Control of Indoor Mold,* Virginia, USA: American Industrial Hygiene Association.

Radonjic, M., Hallam, K. R., Allen, G. C. and Hayward, R. (2001) *Mechanism of carbonation in lime based materials,* translated by Athens, Greece: 465-475.

Raj, P. J. S. (2008) 'Oysters in a new classification of keystone species', *Resonance,* 13(7), 648-654.

Ramachandran, V. S. (1995) *Concrete Admixture Handbook,* 2nd ed., New York, USA: Noyes Publications.

Ramachandran, V. S., Paroli, R. M., Beaudoin, J. J. and Delgado, A. H. (2002) *Handbook of Thermal Analysis for Construction Materials,* New York, USA: Noyes Publication.

Rapp, G. (2009) *Archaeomineralogy,* Duluth, USA: Springer.

Rasanen, V. and Penttala, V. (2004) 'The pH measurement of concrete and smoothing mortar using a concrete powder suspension', *Cement and Concrete Research,* 34(5), 813-820.

Rashid, M. A. and Mansur, M. A. (2005) 'Reinforced High-Strength Concrete Beams in Flexure', *ACI Structural Journal,* 102(3), 462-471.

Reeder, L. (2010) *Guide to Green Building Rating Systems,* Canada: John Wiley & Sons Inc.

Riley, M. A. (1991) 'Possible new method for the assessment of fire–damaged concrete', *Magazine of Concrete Research,* 43(155), 87-92.

Rirsch, E., MacMullen, J. and Zhang, Z. (2011) 'Evaluation of Mortars Samples Obtained From UK Houses Treated For Rising Damp', *Construction and Building Materials,* 25(1), 2845-2850.

Rirsch, E. and Zhang, Z. (2010) 'Rising damp in masonry walls and the importance of mortar properties', *Construction and Building Materials,* 24(10), 1815-1820.

Rochelle, C. A. and Milodowski, A. E. (2004) *Carbonation of borehole seals: Comparing evidence from short-term laboratory experiments and long-term natural analogues* Nottingham, UK: British Geological Survey.

Rojas, M. F. and Cabrera, J. (2002) 'The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin–lime–water systems', *Cement and Concrete Research,* 32(1), 133-138.

Ropp, R. C. (2013) *Encyclopaedia of the Alkaline Earth Compounds,* Oxford, UK: Elsevier B.V.

Rozière, E., Loukili, A. and Cussigh, F. (2009) 'A performance based approach for durability of concrete exposed to carbonation', *Construction and Building Materials,* 23(1), 190-199.

Said, M. N. A. (2006) *Building Envelope, Heating, and Ventilating Practices and Technologies for Extreme Climates PERD-079 - Engineered Building Envelope Systems to Accommodate High Performance Insulation with Outdoor/Indoor Climate Extremes* Ottawa, Ontario, Canada: Institute for Research in Construction National Research Council Canada

Sato, T. and Diallo, F. (2010) 'Seeding Effects of Nano-$CaCO_3$ on the Hydration of Tricalcium Silicates', *Transportation Research Board,* 2141(1), 61-67.

Savas, B. Z. (2000) *Effects on Microstructure on Durability of Concrete*, unpublished thesis North Carolina State University.

Sawada, K. (1997) 'The mechanisms of crystallization and transformation of calcium carbonates ', *Pure and Applied Chemistry,* 69(5), 921-928.

Schroder, L. and Ogletree, V. (2009) 'Adobe Homes for All Climates: Simple, Affordable and Earthquake-Resistant Natural Building Techniques',

Schwarzer, R. A. (2005) 'Texture Mapping by Scanning X-Ray Diffraction and Methods' in Singh, A. K., ed. *Advanced X-Ray Techniques in Research and Industry,* Amsterdam, The Netherlands: IOS Press.

Scott, P. W. and Bristow, C. M. (2002) *Industrial minerals and extractive industry geology,* London: The Geological Society.

Sepulcre-Aguilar, A. and Hernández-Olivares, F. (2010) 'Assessment of phase formation in lime-based mortars with added metakaolin, Portland cement and sepiolite, for grouting of historic masonry', *Cement and Concrete Research,* 40(1).

Sh. Ahmad, S. (2008) 'Kuala Lumpur: A Hot Humid Climate' in Hyde, R., ed. *Bioclimatic Housing: Innovative Designs For Warm Climate*, London, UK: Earthscan Publishing.

Shaffer, N. (2013) *Rocks and Minerals - Calcite*, Indiana, USA: Indiana Geological Survey.

Sheherbakov, D. I. and Belousov, V. V. (2002) *The Interaction of Sciences in the Study of the Earth*, Hawaii, USA: University Press.

Shetty, M. S. (2013) *Concrete Technology: Theory and Practice*, 7th ed., India: S. Chand.

Shonk, J. (2013) *Introducing Meteorology: A Guide to Weather*, Edinburgh: Dunedin Academic Press Limited.

Sickels-Taves, L. B. and Allsopp, P. D. (2005) 'Lime and Its Place in the 21st Century: Combining Tradition, Innovation and Science In Building Preservation', in *International Building Lime Symposium*, Orlando, Florida, USA, NLA Building Lime Group,

Sickels-Taves, L. B. and Sheehan, M. S. (2002) 'Specifying Historic Materials: The Use of Lime' in Throop, D. and Klinger, R. E., eds., *Masonry: Opportunities For The 21st Century*, Salt Lake City, Utah, USA: ASTM.

Siegesmund, S. and Torok, A. (2011) 'Stone in Architecture: Properties and Durability' in Siegesmund, S. and Snethlarge, R., eds., 4th ed., Berlin, Germany: Springer-Verlang Berlin Heidelberg.

Sivakugan, N., Shukla, S. K. and Das, B. M. (2013) *Rock Mechanics: An Introduction*, Florida, USA: Taylor & Francis Group.

Sivakumar, A. and Santhanam, M. (2007) 'Mechanical properties of high strength concrete reinforced with metallic and non-metallic fibres', *Cement and Concrete Composites*, 29(8), 603-608.

Skoulikidis, T., Charalambous, D. and Tsakona, K. (1996) *Amelioration of the properties of hydrated lime for the consolidation of the surface or/and the mass of building materials of monuments or new buildings or statues and ornaments*, translated by Berlin: Elsevier Science.

Skoulikidis, T., Tsakona, K., Vassiliou, P. and Papakonstantinou, P. (1995) 'Consolidation of Stones by Inorganic Solutions Emulsions or Pastes', in Antiquity, A. f. t. S. o. M. a. o. S. I., ed. *4th International Conference of ASMOSIA*, Bordeux, France,

Slocombe, M. (2012) *Traditional Building Materials*, Oxford, UK: Shire Publications.

Smith, A., Highley, D., Bloodworth, A. and Bate, R. (2005) *Natural Hydraulic Lime*, London: British Geological Survey.

Song, H. W., Kwon, S. J., Byun, K. J. and Park, C. K. (2006) 'Predicting carbonation in early-aged cracked concrete', *Cement and Concrete Research*, 36(5), 979-989.

Soriano, L., Monzo, J., Bonilla, M., Tashima, M. M., Paya, J. and Borrachero, M. V. (2013) 'Effect of pozzolans on the hydration process of Portland cement cured at low temperatures', *Cement and Concrete Composites*, 42, 41-48.

Spencer, J. E. and Pearthree, P. A. (2008) 'An evaluation of the evolution of the latest Miocene to the earliest Pliocene Bause lake system in the lower Colorado River Valley, South-western USA' in Reheis, M. C. and Hershler, R., eds., *The Late Cenozoic Drainage History of the South-western Great Basin and Lower Colorado River Region: Geologic and Biotic Perspective,* Colorado: The Geological Society of America.

Stefanidou, M. (2010) 'Methods for porosity measurement in lime-based mortars', *Construction and Building Materials,* 24(12), 2572-2578.

Steffens, A., Dinkler, D. and Ahrens, H. (2002) 'Modelling carbonation for corrosion risk prediction of concrete structures', *Cement and Concrete Research,* 32(6), 935-941.

Stocks, D. A. (2003) *Experiments in Egyptian Archaeology: Stone working Technology in Ancient Egypt,* Oxford, UK: Taylor & Francis.

Stutzman, P. E. (1994) 'Applications of Scanning Electron Microscopy in Cement and Concrete Petrography' in de Hayes, S. M. and Stark, D., eds., *Petrography of Cementitous Materials,* Danvers, USA: American Society for Testing and Materials.

Tahija, D. and Huang, H. H. (2011) 'Fundamental Thermodynamics of Aqueous Carbon Dioxide Systems' in Neelameggham, N. R., Belt, C. K., Jolly, M., Reddy, R. G. and Yurko, J. A., eds., *Energy Technology 2011: carbon Dioxide and Other Greenhouse Gas Reduction Metallurgy and Waste Heat Recovery,* New Jersey, USA: John Wiley & Sons.

Tanabe, T.-a. (2008) 'Influence of Local Climate Conditions on the Carbonation Rate of Concrete' in Tanabe, T., Sakata, K., Mihashi, H., Sato, R., Maekawa, K. and Nakamura, H., eds., *Creep, Shrinkage and Durability Mechanics of Concrete and Concrete Structure,* London, UK: Taylor & Francis Group, 1552.

Tang, Y., Fuh, J. Y. H., Loh, H. T., Wong, Y. S. and L., L. (2003) 'Direct laser sintering of a silica sand', *Materials & Design,* 24(8), 623-629.

Tanyildizi, H. and Coskun, A. (2008) 'The effect of high temperature on compressive strength and splitting tensile strength of structural lightweight concrete containing fly ash', *Construction and Building Materials,* 22(11).

Tasdemir, C. (2003) 'Combined effects of mineral admixtures and curing conditions on the sorptivity coefficient of concrete', *Cement and Concrete Research,* 33(10), 1637-1642.

Tavakkolizadeh, M. and Saadatmanesh, H. (2003) 'Strengthening of Steel-Concrete Composite Girders Using Carbon Fiber Reinforced Polymers Sheets', *Journal of Structural Engineering,* 129(1), 30-40.

Taylor, G. D. (2002) *Materials in Construction: Principles, Practice and Performance,* Essex, UK: Pearson Education Limited.

Taylor, H. F. W. (1997) *Cement Chemistry,* 2nd ed., London: Thomas Telford Publishing.

Teasdale, M. (2005) *Re-pointing: Principles, Materials and Methods,* Hampshire: Hampshire County Council.

Teng, J. G., Smith, S. T., Yao, J. and Chen, J. F. (2003) 'Intermediate crack-induced debonding in RC beams and slabs', *Construction and Building Materials,* 17(6), 447-462.

Teutonico, J. M., Ashall, G., Garrod, G. and Yates, T. (1999) *A comparative study of hydraulic lime-based mortars,* translated by Bartos, P., Groot, C. and Hughes, J. J., Paisley, Scotland: RILEM.

Teutonico, J. M. and English, H. (1997) *The English Heritage directory of building limes : manufacturers and suppliers of building limes in the United Kingdom and the Republic of Ireland*, Shaftesbury: Donhead.

Teutonico, J. M., McCaig, I., Burns, C. and Ashurst, J. (1993) 'The Smeaton Project: Factors Affecting thr Properties of Lime-Based Mortars', *APT Bulletin*, 18(44), 18.

Thomas, J. J., Jennings, H. M. and Chen, J. J. (2009) 'Influence of Nucleation Seeding on the hydration Mechanism of Tricalcium Silicates and Cement', *The Journal of Physical Chemistry*, 113 (11), 4327-4334.

Thomas, M. D. A., Cail, K., Blair, B., Delagrave, A., Masson, P. and Kazanis, K. (2010) 'Use of Low-CO2 Portland Limestone Cement for Pavement Construction in Canada', *International Journal of Pavement Research & Technology*, 3(5), 228.

Tokchom, S., Ghosh, P. and Ghosh, P. (2009) 'Effects of Water Adsorption, Porosity and Sorptivity on Durability of Geopolymer Mortars', *ARPN Journal of Engineering and Applied Science*, 4(7), 28-32.

Toney, M. F. (1992) *X-Ray Diffraction, Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films*, Massachusetts, USA: Butterworth-Heinemann.

Tongamp, W., Kano, J., Zhang, Q. and Saito, F. (2008) 'Simultaneous treatment of PVC and oyster-shell wastes by mechanochemical means ', *Waste Management*, 28(33), 484-488.

Toprak, G. (2007) *CHARACTERISTICS OF LIMES PRODUCED FROM MARBLES AND LIMESTONES*, unpublished thesis İzmir Institute of Technology.

Topçu, I. B., Bilir, T. and Uygunoğlu, T. (2009) 'Effects of waste marble dust as filler on properties of self-compacting concrete', *Construction and Buolding Materials*, 23(5), 1947-1953.

Torney, C. (2013) *Investigating Restoration Mortars*, Edinburgh: Historic Scotland.

Torney, C., Forster, A. M. and Szadurski, E. M. (2014) 'Specialist ‘restoration mortars’ for stone elements: a comparison of the physical properties of two stone repair materials', *Heritage Science*, 2(1), 1-12.

Trewin, N. H. and Davidson, R. G. (1999) 'Lake-level changes, sedimentation and faunas in a Middle Devonian basin-margin fish bed', *Journal of the Geological Society*, 156(3), 535-548.

Trumbull, W. C. (1999) 'The Chicago Brownfield Initiative' in Kibert, C. J., ed. *Reshaping the Built Environment: Ecology, Ethics and Economics*, Washington DC, USA: Island Press.

Un, H. and Baradan, B. (2011) 'The effect of curing temperature and relative humidity on the strength development of Portland cement mortar', *Scientific Research and Essays*, 6(12).

Urquhart, D. (2013) *Historic Concrete in Scotland Part 1: History and Development*, Edinburgh: Historic Scotland.

Uyeda, C. (2009) *Australian Master Environment Guide*, Australia: CCH Australia Limited.

Uysala, M. and Tanyildizi, H. (2012) 'Estimation of compressive strength of self compacting concrete containing polypropylene fiber and mineral additives exposed to high temperature using artificial neural network', *Construction and Building Materials,* 27(1), 404-414.

Valek, J. and Matas, T. (2012) 'Experimental Study of Hot Mixed Mortars in Comparison with Lime Putty and Hydrate Mortars' in Valek, J., Hughes, J. J. and Groot, C. J. W. P., eds., *Historic Mortars: Characterisation, Assessment and Repair,* UK: Springer.

Van Balen, K. (2005) 'Carbonation reaction of lime, kinetics at ambient temperature', *Cement and Concrete Research,* 35(4).

Van Balen, K. and Van Gemert, D. (1994) 'Modelling Lime Mortar Carbonation', *Materials and Structures,* 27(7), 393-398.

Veltman, K., Singh, B. and Hertwich, E. G. (2010) 'Human and Environmental Impact Assessment of Postcombustion CO2Capture Focusing on Emissions from Amine-Based Scrubbing Solvents to Air', *Environmental Science and Technology,* 44(4), 1496-1502.

Ventolà, L., Vendrell, M. and Giraldez, P. (2013) 'Newly-designed traditional lime mortar with a phase change material as an additive', *Construction and Building Materials,* 47(2013), 1210-1216.

Vicat, L. J. (1997) *Mortars and cements,* Shaftesbury: Donhead.

Vicat, L. J. and Wingate, M. (1997) *Mortars and cements,* Reprinted ed., Shaftesbury: Donhead.

Virdi, S. (2012) *Construction Science and Materials,* West Sussex, UK: John Wiley & Sons Ltd.

Vitruvius, P. (2013) *Vitruvius, the Ten Books on Architecture,* New York, USA: Hardpress Publishing.

Wada, N., Yamashita, K. and Umegaki, T. (1995) 'Effects of divalent cations upon nucleation, growth and transformation of calcium carbonate polymorphs under conditions of double diffusion', *Journal of Crystal Growth,* 148(3), 297-304.

Walker, M. (2002) *Guide to the Construction of Reinforced Concrete in the Arabian Peninsula,* UK: The Concrete Society.

Wang, L. K., Pereira, N. C. and Chen, W.-Y. (2004) *Air pollution control engineering,* Totowa, N.J.: Oxford : Humana ; Blackwell.

Wang, P. M. and Liu, X. P. (2011) 'Effect of temperature on the hydration process and strength development in blends of Portland cement and activated coal gangue or fly ash', *Journal Of Zeijiang University - Applied Physics and Engineering,* 12(2), 162-170.

Ward-Harvey, K. (2009) *Fundamental Building Materials,* 4th ed., Florida, USA: Universal Publishers.

Weerakoon, W. M., Olszyk, D. M. and Moss, D. N. (1999) 'Effects of nitrogen nutrition on responses of rice seedlings to carbon dioxide', *Agriculture, Ecosystem & Environment,* 72(1), 1-8.

Wei, H., Shen, Q., Zhao, Y., Wang, D. J. and Xu, D. F. (2003) 'Influence of polyvinylpyrrolidone on the precipitation of calcium carbonate and on the transformation of vaterite to calcite', *Journal of Crystal Growth,* 250(3), 516-524.

Weismantel, G. E. (1999) 'Whiting (Calcium Carbonate)' in McKetta, J. J., ed. *Encyclopaedia of Chemical Processing and Design*, Basel, Switzerland: Marcel Dekker Inc.

Wen, Y., Xiang, L. and Jin, Y. (2003) 'Synthesis of plate-like calcium carbonate via carbonation route', *Materials Letters*, 57(16-17), 2565-2571.

West, T. O. and McBride, A. C. (2005) 'The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions ', *Agriculture, Ecosystems and Environment*, 108(2005), 145-154.

Wilkinson, S. (2009) *A Study of the Moisture Buffering Potential of Hemp in Combination with Lime and Clay-Based Binders* unpublished thesis University of East London.

Winegardner, D. L. (1995) *An Introduction to Soils for Environmental Professionals*, Florida, USA: Lewis Publishers.

Wingate, M., Sakula, J. and Hill, N. (1985) *Small-scale lime-burning : a practical introduction*, London: Intermediate Technology.

Winnefeld, F. and Böttger, K. G. (2006) 'How clayey fines in aggregates influence the properties of lime mortars', *Materials and Structures*, 39(4), 433-443.

Wise, K. J. (1997) *Precipitated calcium carbonate particles from basic calcium carbonate*,

Wong, H. S., Buenfeld, N. R. and Head, M. K. (2006) 'Estimating transport properties of mortars using image analysis on backscattered electron images', *Concrete and Cement Research*, 36(8), 1556-1566.

Wu, W., Hea, T., Chen, J. F., Zhang, X. and Chen, Y. (2006) 'Study on in situ preparation of nano calcium carbonate/PMMA composite particles', *Material Letters*, 60(19), 2410-2415.

Yang, E. I., Kim, M. Y., Park, H. G. and Yi, S. T. (2010) 'Effect of partial replacement of sand with dry oyster shell on the long-term performance of concrete', *Construction and Building Materials*, 24(5), 758-765.

Yang, F., Zhang, B. and Ma, Q. (2011) 'Study Of Sticky Rice-Lime Mortar Technology For The Restoration Of Historical Masonry Construction', *Account of Chemical Research*, 43(6).

Yates, T. and Ferguson, A. (2008) 'The Use Of Lime Based Mortars In New Build ',

Yau, Y. H., Chew, B. T. and Saifullah, A. Z. A. (2012) 'Studies on the indoor air quality of Pharmaceutical Laboratories in Malaysia', *International Journal of Sustainable Development*, 1(1), 110-124.

Yeomans, D. (1997) *Construction Since 1900: Materials*, Somerset, UK: B.T. Batsford Ltd.

Yoon, G. L., Kim, B. T., Kim, B. O. and Han, S. H. (2003) 'Chemical–mechanical characteristics of crushed oyster-shell', *Waste Management*, 23(9), 825-834.

Yoon, H., Park, S., Lee, K. and Park, J. (2004) 'Oyster Shell as Subsititute of Aggregates in Mortar', *Waste Management & Research*, 22(3), 158-170.

Yudelson, J. (2007) *Green building A to Z [electronic resource] : understanding the language of green building*, Gabriola Island, BC: New Society Publishers.

Zhang, Z., Xie, Y., Xu, X., Pan, H. and Tang, R. (2012) 'Transformation of amorphous calcium carbonate into aragonite', *Journal of Crystal Growth*, 343(1), 62-67.

Zhong, B. Y., Zhou, Q., Chan, C. F. and Yau, Y. (2012) 'Structure and Property Characterization of Oyster Shell Cementing Material ', *Chinese Journal of Structural and Chemistry*, 31(1), 85-92.