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THE EFFECT OF EXTENDING FOUR CEMENTS WITH LIMESTONE WITH ADDITION OF SUPER-PLASTICISERS ON THE HYDRATION REACTION OF SCC CEMENT PASTE

by

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Declaration

I, Rihab Abdelrahman Mohamed Elmakki, declare that the contents of this dissertation represent my own unaided work, and that the dissertation has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

17/ 08/ 2016

Signed

Dated

Abstract

The addition of certain fillers and additives in conventional concrete is imperative for improving its rheological properties. The effect of additives, namely limestone (LS) and superplasticisers (SP), on the hydration kinetics of self-compacting concrete (SCC) was investigated on cement paste scale. These additives interact mostly with cement paste, since aggregates are considered to be inert materials. An understanding of the effect of these additives on the hydration kinetics of cement paste is paramount to the design of an SCC with excellent properties.

Four CEM I 52.5N Portland cements from one supplier but produced at different factories, LS and two types of SP, were used in this research. The hydration kinetics were evaluated by monitoring the elastic modulus growth of the cement pastes. Different coefficients of the self-acceleration kinetics equation – the self-acceleration constant, characteristic time and real time of hydration – were used to establish the effect of different concentrations of SP with and without the optimum concentration of limestone (30%) on the hydration kinetics of cement pastes. As far as can be ascertained, this is the first time the rheokinetic model has been used to describe the initial hydration of SCC paste.

The results showed that each cement exhibited different rheological properties due to the variations in their physical and chemical compositions. In general, cements with high self-acceleration constant (K) and characteristic time (Θ) values resulted in a low hydration rate, whilst those with low values exhibited a high hydration rate. In particular, the presence of SP in cement pastes increased the K and Θ values during hydration. SP1 showed a greater effect on the rate of hydration than SP2 as the values of the self-acceleration coefficients of cement pastes with SP1 were higher than those with SP2.

It was observed that an increase in the concentration of the two types of superplasticisers (SP1 and SP2) affected the rate of hydration by increasing the hydration time of both blended and unblended limestone cement pastes. Moreover, the addition of limestone in cements with SP significantly increased the hydration time by drastically decreasing the hydration rate resulting in the lowest hydration rate. This was attributed to the interaction between SP, C_3A and sulphate which mostly affects the hydration rate of cement paste. It was also noted that when limestone was used with SP, the hydration reaction was highly dependent on the C_3A content in cements, since a higher amount of C_3A leads to a stronger reaction with $CaCO_3$ to form mono-carbonate.

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- And lastly, the love of my life, my husband, who showered me with support, love and patience, without whom I would have never accomplished this.

Dedication

This thesis is dedicated to my mother. Though she is no longer with us, her love and memories have been a great source of strength in my times of weakness.

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Nomenclature

Constants

A_o	Initial chemical affinity of cement hydration	J/m^3
A_a	Chemical affinity of cement hydration	J/m^3
Blaine	Value of the Blaine fineness	m^2/kg
c	Constant characterising the self-acceleration effect	-
E_a	Apparent activation energy	J/mol
G'	Storage modulus	Pa
G''	Loss modulus	Pa
G^*	Complex modulus	Pa
k	Parameter of the hydration kinetics model	J
K	The constant of the initial reaction rate	-
M_{ce}	Amount (by mass) of cement in the paste	kg/m^3
n	Function of na and a	$ln(J\times hr)$
p	Applied pressure	Pa
p_{atm}	Atmospheric pressure	Pa
q_{ace}	Specific heat of the anhydrous cement	$J/(kg\times K)$
q_{hce}	Fictitious specific heat of the hydrated part of cement	$J/(kg\times K)$
q_{paste}	Specific heat of cement paste	$J/(kg\times K)$
q_w	Specific heat of water	$J/(kg\times K)$
R	Universal gas constant	$J/(kg\times K)$
R_h	The relative rate of hydration or the speed of the reaction	-
S	Function of p and a	-
T	Temperature	K
T^*	The complete rigidification time	s
t	Time	s
x	Dimensionless storage modulus	-

Greek letters

α	Degree of hydration	-

α_u	Ultimate degree of hydration	-
β	Degree of conversion	-
γ	Shear strain	%
δ	Phase shift	-
ε	Constant of self-deceleration	-
η_α	Normalised permeability of the hydration products	$1/(J\times hr)$
θ	Characteristic time	s
ν	Volume ratio between the hydration products and the	-
v_{293}	Volume ratio between the hydration products and η	-
τ	Shear stress	Pa
ω	Angular velocity	s^{-1}
ρ_{paste}	Density of cement paste	kg

Terms and concepts

AFM	Monosulphate (Hydration product)
AFT	Ettringite (Hydration product)
C	Cement
Characteristic time	Total time that hydration would normally take
Clinker	The main component of cement in the manufacture of ordinary
Coagulation	Product of the gelation of the cement paste which has a poor
Complex modulus	Combination of viscous and elastic behaviour of a material
C-S-H	Calcium silicate hydrate
CSP	Concentration of superplasticiser
DTG	Derivative thermogravimetric
Elasticity	The material property of returning to an initial form or state
Hydration	Reaction of cement paste with water
HWRA	High range water reducing admixture (superplasticiser)
Kinetics	The study of rates of chemical processes and the factors that
LAOS	Large amplitude oscillatory shear
LS	Limestone
LVR	Linear viscoelastic region
OPC	Ordinary Portland cement
PCE	Polycarboxylate, a type of superplasticisers
PEO	Polyoxyethyleneside chains of polycarboxylate-type
PLS	Lignosulphonates, a type of superplasticiser
PPC	Pretoria Portland Cement Co.
PSD	Particle size distribution
Real time of hydration	Actual time that the hydration reaction takes
Rheology	Science of deformation and flow
Rheometer	Device used for rheological measurements under different
SAOS	Small amplitude oscillatory shear
Self-acceleration kinetics	Mathematical models describing the self-acceleration mechanism
Self-compacting concrete	A highly flowable concrete that does not require any type of
Self-compacting paste	A cement paste which constitutes the main component of self-
SEM	Scanning electron microscopy

Setting	Cement transition from paste to hard solid
Setting time	Time required for the cement mixture to set
SMF	Sulphonated Melamine Formaldehydes, a type of superplasticiser
SNF	Sulphonated Naphthalene Formaldehydes, a type of
SP	Superplasticiser
Superplasticiser	A chemical admixture that can be added to concrete mixtures to
Strain	Relative deformation
TGA	Thermogravimetry
Viscoelastic	Material behaviour which is simultaneously viscous and elastic
Viscous	Flow resistance or deformation resistance
Viscosity	The material property to resist deformation
VMA	Viscosity modifying agent
w/c	Water cement ratio
XRD	X-ray diffraction
Yield stress	Minimum shear stress required to initiate or maintain a flow

Chapter 1. Introduction

As a flowable concrete, self-compacting concrete (SCC) is able to consolidate under its own weight. SCC, developed in 1988 in Japan, was initially regarded as the technology of the decade. It has been used in South Africa for more than a decade but due to the complex nature of the material and its sensitivity to variation in materials and add-mixtures, it has not been used extensively. The performance of SCC is highly dependent on the rheological properties of self-compacting concrete paste (SCCP) systems. Paste is the vehicle of aggregate transportation during the flow of SCC. SCC is characterised as a non-Newtonian fluid and rheology provides appropriate tools to gain an understanding of the hydration and how different constituents affect SCCP. However, there is still a lack of understanding concerning the effect of additives and substitution of extenders in the paste systems on the hydration of SCC, despite several studies conducted on this topic. This research, therefore, investigates the effect of extending cement by limestone, in the presence of superplasticisers at different dosages, on the hydration of SCCP.

1.1 Background and Motivation

SCC is a concrete that is able to flow under its own weight, thus filling the formwork while simultaneously exhibiting great resistance to segregation (Okamura & Ouchi, 2000; Brouwers & Radix, 2005; Ling & Kwan, 2015).

Due to this high flowability, its placement can be achieved without any means of vibration and SCC finds wide use in applications with difficult casting conditions, for instance, in densely reinforced concrete and/or complex shapes (Schwartzentruber *et al*., 2006).

Better performance of SCC is achieved by addition of mineral and chemical additives, such as limestone (LS) and superplasticisers (SP), to improve the rheological properties of the cement paste (Sahmaran *et al.,* 2006). Limestone improves the viscosity of the cement paste, thereby allowing transportation of the aggregate as a composite material within the concrete without segregation (Khayat, 1999; Shen *et al.,* 2015). The yield stress of cement paste decreases upon addition of SP thereby improving the flowability of the concrete (Mbasha *et al.,* 2015).

The hydration of cement paste determines the properties of fresh and hardened SCC (Nagaratnam et al., 2016; Juilland *et al.,* 2010). The overall rigidification process of the cement paste, hence its workability, is affected by changes in the paste microstructure which occur as a result of stronger forces of attraction between cement particles during hydration. The formation of hydrate products, such as calcium-silicate hydrate (C-S-H), has been cited as one of the major reasons for the rigidification of cement paste (Bellotto, 2013). It is therefore clear that cement hydration dictates the rheological properties of cement (Hildago *et al*., 2008).

The effect of LS on the hydrate products, particularly on the monocarbonate, has been investigated using various techniques (Lothenbach *et al.,* 2008; Celik *et al.,* 2015). The monocarbonate stabilises ettringite around the most reactive cement compound (C_3A). According to Klemm and Adams (1990), ettringite formation has rapid kinetics. However, the effect of LS on the formation of ettringite is still not fully understood. It has been reported by some researchers that the presence of LS retards ettringite formation (Tsivilis *et al.,* 1998; Kakali *et al.,* 2003), though the opposite was observed by Ingram *et al.* (1990) and Ramachandran (1988). It was also observed that for cements with a higher C_3A content, an increase in the quantity of LS increased the amount of monocarbonate (Barker & Cory, 1991) and it was concluded that the hydration rate of Portland cement was accelerated by LS (De Schutter, 2011). This was attributed to the increased possibilities of nucleation caused by the LS filler, due to shortened induction period of the reaction. In contrast, it was deduced that LS has no effect on the later stages of hydration, only affecting the early stages (Hooton *et al.,* 2007).

The effect of SPs on the hydration reaction of LS blended cement has also been reported in literature. The addition of polycarboxylate SPs led to a significant reduction of the hydration rate in LS blended cement (Moratti *et al.,* 2012).From the above it can be seen that certain ambiguities remain over the effect of limestone on the initial hydration in the literature. Therefore, this research intends to investigate the influence of cement characteristics, LS and SP on cement paste rheology during early hydration.

1.2 Aim and delineation

The main objective of this research was to investigate the effect of LS and SPs on the hydration kinetics of cement paste, focusing on the rigidification process in the dormant phase. Furthermore, the aim of this work was to find a model that best describes the growth of the elastic modulus as a function of time, and which correlates the coefficients of the model to characterise the effect of these additives on the hydration of SCCP.This study considered the hydration process of four different local cement pastes: limestone and two types of polycarboxylate-based superplasticisers. The flow properties and the durability properties of cement paste were not investigated.

1.3 Objectives and outcomes

During experimental work, the following will be investigated:

- The evolution of elastic moduli of cement pastes at different SP concentrations over time to assess the effect of SP type and dosage on the kinetics of cement paste hydration.
- The evolution of elastic moduli of cement pastes with and without limestone at different SP concentrations.
- The application of self-acceleration kinetic equation to follow the evolution of elastic moduli as a function of hydration on the cement paste rigidification.

From the self-acceleration kinetic equation, three main coefficients could be used to characterise the rheological behaviour of these cements:

- The self-acceleration constant *(K)* that defines the rate of hydration.
- The characteristic time *(Ө)*that determines the total time of the dormant phase.
- The real time *(T*)* that defines the rigidification time of cement paste during experiment.

These coefficients make the comparison between the different cement compositions and the effect of LS and SPs on the hydration kinetics more quantitative-based and more definite.

1.4 Assumptions

During the experimental work it was assumed that the stress was equally distributed over the sample between the plates of the rheometer. Moreover the particle distribution of cement grains was assumed to be the same in all samples used.

1.5 Significance

A great deal of effort has been invested towards investigating and gaining an in-depth understanding on the rheological behaviour of SCC during the hydration process. However, the lack of SCC specifications and understanding of its rheological behaviour during the initial hydration phase, sensitivity to changes in w/c ratio and variation in constituent materials, has led to its limited acceptance and sparse use within the local construction industry in South Africa. This research applied the self-acceleration kinetic model to investigate the rheological behaviour of SCCP using different local materials during early hydration. This kinetic model, adapted from polymer science (Malkin & Kulichikhin, 1996), was applied to SCC for the first time, thereby contributing to the current SCC knowledge.

1.6 Methodology

All experiments were conducted using cement pastes with and without the addition of limestone (LS) at variant superplasticiser (SP) concentrations. Four CEM I 52.5N Portland cements from one supplier but produced at different factories, LS and two types of SP, were used in this research.A non-destructive method (i.e., dynamic mode rheology) was used to avoid modification of the microstructure of cement paste. The effect of cement hydration was monitored within the linear viscoelastic zone using the oscillatory technique on an MCR51 rheometer. The growth of elastic modulus using time sweep measurements at a constant frequency of 1 Hz and a constant strain of 0.2% were carried out at 25 °C for all the cement pastes.

1.7 Organisation of dissertation

Chapter 2: Literature Review

Only a few studies have been published on the rheology of self-compacting concrete (SCC) in general, and on self-compacting concrete paste (SCCP) in particular. This chapter reviews the following concepts: rheology, cement paste, superplasticiser, limestone and hydration. The effect of hydration on cement paste rheology is reviewed in depth. Different hydration kinetics models for describing the hydration process are presented.

Chapter 3: The Experimental Procedures

This chapter describes the methodology adopted in detail. The importance of carrying out the experiments in dynamic mode rheology or oscillation mode is highlighted. Additionally, the measurement parameters adopted in the research are introduced.

In order to determine the evolution of the coagulating cement paste, it was necessary to observe the development of its elastic modulus over time. From these time-dependent results from the rheometer, rheokinetics coefficients were able to be estimated, including self-acceleration kinetics, characteristic time and real time.

Chapter 4: Results and Discussion

The data obtained experimentally are presented and discussed in this chapter. Each rheokinetic coefficient is presented for all cements under different conditions. The effects of SP dosage and the addition of limestone on cement paste hydration were evaluated. The observed rheological behaviour of all cements is correlated to their physical and chemical characteristics.

Chapter 5: Summary, Conclusions and Recommendations

A brief summary of the work conducted is provided in this chapter based on the outcomes of the project. Recommendations are made for work that remains to be done to improve existing knowledge on the effect of limestone and superplasticiser on the hydration of ordinary Portland cements

Chapter 2. Literature review

The effect of superplasticiser and limestone on the rheological properties of the self-compacting concrete paste (SCCP) is the main focus of this research. This chapter will introduce the relevant theories regarding the rheology of self-compacting concrete paste (SCCP). A background on rheology and main rheological concepts are presented, with particular emphasis on dynamic oscillatory shear tests. The hydration reaction of cementitious material will be discussed in general, with a special focus on cement paste. Chemical and mineral admixtures such as superplasticisers and limestone are reviewed considering their effect on self-compacting concrete paste.

2.1 Self-compacting concrete

According to Ling and Kwan (2015), self-compacting concrete (SCC) is defined as a highly flowable concrete that does not require any type of vibration for its placement (Figure 2.1). It offers many advantages to the concrete industry in terms of economy, technic and environment (Walraven, 2003). Self-compacting concrete also has a high deformability while exhibiting a great resistance to segregation. These two major properties of SCC (flowability and segregation resistance) have made this construction material very popular worldwide. SCC has application in cases of difficult casting conditions such as densely reinforced concrete or in complex shapes.

Figure 2-1: Self compacting concrete
(Adapted from Sika, 2016)

However, some problems may occur when handling self-compacting concrete during construction: segregation, bleeding or settlement, for example. Segregation can appear during placement (dynamic segregation) or after placement during the dormant period (static segregation) (Schwartzentruber *et al.,* 2006).According to Sahmaran *et al.* (2006), the remedy to these problems would be the improvement of concrete rheological properties such as yield stress and viscosity, achieved by increasing the fine aggregate content, controlling the maximum aggregate size, adding high range water reducing admixture (HWRA), increasing the powder content or using viscosity modifying agents (VMA). The cost factor involved in the production of SCC (because SCC requires more cement and chemical add mixtures) has given rise to the alternative of using mineral additives (more often fine materials) such as limestone, limestone powder and fly ash as cement replacements/extenders. These additions improve not only the fresh properties of concrete but also the hardened properties.

Sahmaran *et al.* (2006) found that the workability of SCC depended on the type of SP used and that the polycarboxylate type provided improved workability. The particle size and distribution of mineral additives, though an important factor, is not the only property improving the workability of concrete. Other properties such as surface characteristics and the spherical shape of some of the additives, fly ash for example, can also affect workability. The replacement of cement by some additives affects the setting time and can sometimes result in a decrease of strength (Sahmaran *et al.,* 2006).

Though SCC is not expected to completely replace conventional concrete, its use is expected to increase as more and more companies demand a higher quality product that is easier to use. According to Nagaratnam *et al.* (2016), the performance of self-compacting concrete (fresh or hard) is highly dependent on the rheological properties of self-compacting concrete paste (SCCP) phase during hydration. In fact, the increase in the magnitude of attractive forces between cement particles during hydration results in microstructural changes within the paste. This, then, affects the overall rigidification process of cement paste and thus its workability. Therefore, this project will focus primarily on the cement paste (Banfill, 2003).

2.1.1 Cement paste

Cement paste is the "glue" in concrete and consists of cement, water (pure cement paste) and most often with some chemical admixtures such as superplasticiser, some supplementary cementitious materials such as fly ash and burnt furnace slag and limestone powder.

Cement

Cement is a complex material consisting of various mineralogical compounds in various proportions. The characterisation of cement can be done by specifying its chemical compositions, its mineral compositions and its physical characteristics.Based on its chemical composition, Portland cement mainly comprised of CaO at about 60% of the cement, 20% of

SiO_2, 5% of Al_2O_3, 3.3% of Fe_2O_3, 3.5% of SO_3 and about 2.36% of MgO. Many other elements exist in the form of impurities such as oxides of calcium, potassium, sodium, carbon and chloride (Mukhopadhyay & Jang, 2009).

The following short hand notation is used by cement chemists:
Al_2O_3 → [A] CaO → [C] Fe_2O_3 → [F] SiO_2 → [S]
Na_2O → [N] SO_3 → [S$^-$] H_2O → [H]

Based on its physical characteristics, Portland cement consists of grains of different sizes with those less than 24 Mm and 34 Mm representing the highest proportion with up to 94% of the total.The mineral composition of Portland cement has been classified by Zhang *et al.* (2010a) as follows: Alite (C_3S) representing about 65% of the mixture, Belite (C_2S) about 15%, Ferrite about (C_4AF) 7.7% and cubic aluminate (C_3A) 5.9%. These four main cement compounds are formed through thermal reaction in the burning clinker whilst the gypsum ($CaSO_4$) is added to the mill during the grinding process of the cement clinkers.

C_3S [Alite]: Ca_3SiO_5 C_3A [Aluminate]: $Ca_3Al_2O_6$
C_2S [Belite]: Ca_2SiO_4 C_4AF [Ferrite or Brownmillerite]: $Ca_4Al_2Fe_2O_{10}$

The clinker mineralogy can be determined by Bogue calculations or by Rietveld analysis of X-ray diffractograms (XRD). The latter is preferable due to its exactitude in estimation compared to the result provided by the former technique (Vikan, 2005). There are a number of methods for estimating these cement compounds. The Bogue method has been used under specified conditions. However, it has been reported that the Bogue calculations provided cement compounds that differ remarkably from the actual phase compositions. This method underestimates alite and ferrite and overestimates belite and aluminate, occurring mainly when the clinker in the kiln did not reach the required thermal equilibrium (De La Torre *et al*., 2002).

Superplasticiser

Superplasticisers, used as high range water reducing admixture (HWRA) or dispersing admixture, are mostly incorporated into concrete mixtures to improve the fresh properties (workability) and sometimes the hardened properties. These admixtures influence the rheology of cement paste in such a way that the yield stress and viscosity of cement paste can be reduced depending on the type and dosage of superplasticiser used (Koehler, 2009; Mbasha *et al.,* 2015). Classification based on chemical compositions of superplasticisers have been reported by various authors with Lignosulphonates (PLS), Sulphonated Melamine Formaldehydes (SMF), Sulphonated Naphthalene Formaldehydes (SNF), and Polycarboxylic Ethers (PCE) cited as a few types of SP (Rixom & Maivaganam, 2003).

According to Banfill (2003), the adsorption process of superplasticiser on cement particles takes place in three stages. The first stage is characterised by the consumption of superplasticisers through intercalation, co-precipitation and micellisation. The second stage consists of the adsorption of the additive onto the surface of the cement particles. This is followed by the final stage where some of the superplasticisers remain in the solution which plays a role in dispersing the flocks.The purpose of SP in industry is to improve the concrete workability at low water/cement ratio. The use of SP in cementitious materials not only offers physical advantages but also provides economic advantages. In fact, the production cost of cement is exceedingly lowered since its content can be optimised in the concrete mixture when using SP (Puertas *et al.,* 2005).

According to Puertas *et al.* (2005), the usage of superplasticisers as dispersive admixtures dates from the 1930s. In the early 1960s, sulphonatedmelanine formaldehydes and naphthalene were developed in Germany and Japan, respectively. This marked a significant progress in the understanding of SPs, allowing concrete engineers to use SPs with greater understanding and under specific conditions.The need to improve the effectiveness of SPs led researchers to develop a different type of superplasticiser based on Polycarboxylate rather than melamine or naphthalene (Puertas *et al*., 2005).

Research conducted by Zhang *et al.* (2010b) show that superplasticisers owe their effectiveness on the dispersing effect done on cement particles by preventing them to agglomerate. According to Pumphrey (2012), when cement is mixed with water, the particles of the cement are attracted to each other, leading to a thickening of the mixture. The addition of superplasticiser, which attacks cement particles and results in a highly negative charge, causes particles to repel. Therefore, cement paste remains for a while in the liquid phase. Figure 2.2 explains the function of superplasticiser on cement.

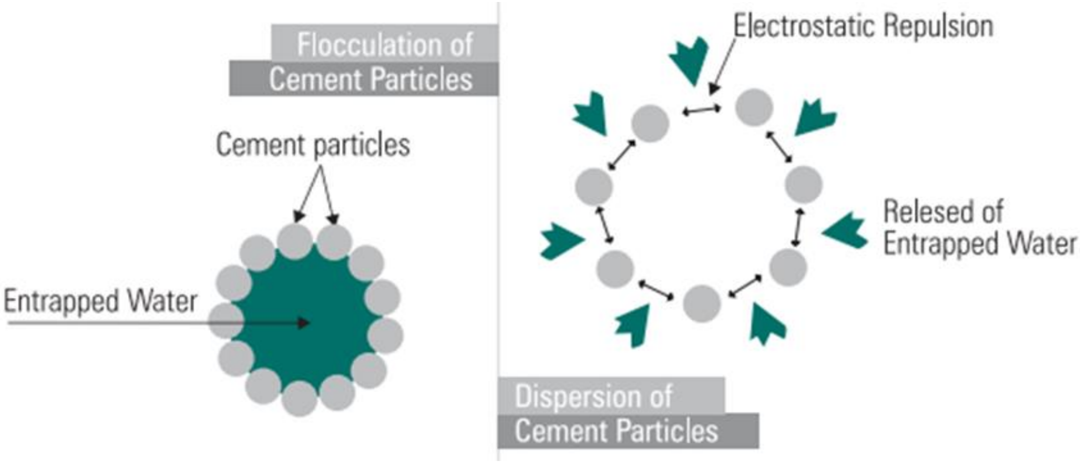

Figure 2-2:Function of superplasticiser (Adapted from Apple Chemie, n.d)

Polycarboxylate type SPs

Polycarboxylate (PCE) based superplasticisers were first developed about 30 years ago in Japan. They have a large capacity to reduce water and cement content through electrostatic repulsion and steric effect. Figure 2.3 shows the function of Polycarboxylic (PCE) type of superplasticiser in cement paste. The fluidity of cement paste when used with PCE SPs is maintained longer as compared to other types of polymers without excess retardation. New types of PCE SPs have been developed which induce high fluidity, viscosity and shrinkage reducing capacities, used mainly for high and ultra-high strength concrete (Takemoto, n.d).

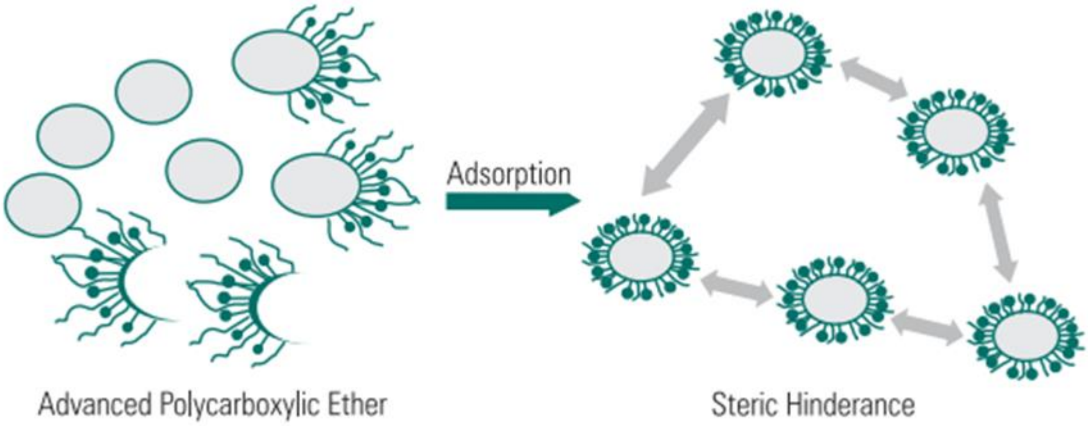

Figure 2-3:Function of Polycarboxylate ether type superplasticiser(Adapted from Apple Chemie, n.d)

Puertas *et al*. (2005) found that the difference between polycarboxylate and other SP types lies in their molecular structures. A polycarboxylate SP is formed normally of one main long linear chain on which small lateral chains, consisting of carboxylates and ethers group, are attached. These lateral carboxylate chains have been shown to increase the ability of SPs to be adsorbed on the surfaces of the cement particles. The quality and the duration of fluidity is highly related to the amount and the length of both the main and the lateral chains. A shorter main chain with longer and numerous lateral chains was related to higher and lasting fluidity. Besides the nature of the main and lateral chains, molecular weight is an important factor in the performance of SP in cement paste. High absorption and degree of flowability are achieved with SP having greater molecular weight (Puertas *et al*., 2005).

Yamada *et al.* (2000) investigated the impact of the side chain length and polymerisation degree of the main chain. They deduced that longer polyoxyethylene (PEO) side chains of polycarboxylate-type superplasticisers were associated with higher liquidity at the same dosage as compared to shorter chains. The fluidity associated with longer side chains decreased over time and the setting time was shorter. Furthermore, a shorter main chain was shown to lead to higher fluidity, a longer setting time and higher concrete durability. These researchers concluded that SPs would reduce the rheological parameters of the cement paste (yield stress and the plastic viscosity) depending on the value of w/c ratio.

Limestone

Limestone, a sedimentary rock consisting mainly of primary carbonate ($CaCO_3$) occurring as mineral calcite, is commonly found in clear, shallow waters. It is generally formed from the accumulation of various materials such as shell, coral, algal and faecal debris. In some cases, the precipitation of calcium carbonate, generally from lake or ocean water, can also cause its formation (Geology, n.d.).

There are various ways to classify limestone as described in literature: by the grain type and grain size, or by their depositional texture. The use of limestone as a filler in cement paste has escalated in recent years due to several advantages over ordinary cements. Limestone has 50% of calcium carbonate expressed as Calcite by weight. Other materials such as quartz, feldspar, clay minerals, pyrite, and siderite are present but in small amounts.Esping (2008) found that the specific surface area of limestone had a great impact on the flowability of cement paste: the higher the specific surface area, the greater the viscosity and yield stress. The loss of flowability over time is significant as determined by slump flow. Thus, the yield stress values changed significantly over hydration time whereas the viscosity changed only slightly with time.

Rubio-Hernandez *et al*. (2013), using self-compacting concrete paste with limestone, reported that the addition of a small amount of limestone led to a decrease in yield stress while a higher concentration caused an increase in yield stress. This observation was explained as follows: when the limestone concentration is small, there are only a few limestone particles in the mixture. Limestone particles do not interact with superplasticisers and due to their smaller size, as compared with cement particles, they occupy the interstices between various cement particles, decreasing the microstructure.

A further investigation by Rubio-Hernandez *et al*. (2013) showed a decrease in the plastic viscosity of the cement paste with increasing limestone content. A paste with higher limestone content showed a higher risk of segregation of concrete due to the incapacity of the particles to aggregate and form a network. Therefore, it can be concluded that the addition of limestone reduces plastic viscosity which increases the risk of segregation (Vikan *et al.,* 2007). Research by Shen *et al.* (2015) determined that limestone increased the viscosity of the self-compacting concrete paste to transport the aggregate within the concrete as a composite material (e.g. resisting segregation).

2.2 Hydration of cement paste

Hydration of cement paste is the process by which water is added to cement powder to produce a liquid suspension which progressively hardens into a porous solid over a few hours and develops further strength over days and months (Juilland *et al*., 2010).Kirby and Lewis (2002) showed that the irreversible stiffening of the paste at the beginning of the acceleration period is due to the effects of hydration and that the hydration phenomenon influences both the colloidal forces during the early stages and the initial setting. These facilitated solid bridge formations.

Understanding the cement hydration process is an important aspect of the rheology of cement paste and the interaction with other admixtures. Whilst many believe that no hydration occurs in the ‘dormant’ period, some hydration products grow considerably on the cement grains surface during this period. The hydration of cement paste occurs in different stages and at different rates (Kirby & Lewis, 2002).

Tricalcium aluminate/ Tetracalcium Aluminoferrite

Tricalcium aluminate (C_3A) has a high reactivity to the water during initial hydration. The crystal structure of C_3A, particularly its cubic formation, has the ability to change in the presence of impurities due to the isomorphous replacement of Ca^{2+} and Al^{3+} by some ions such as Na, K, Mg, Fe, Si, Mn, Ti and Cr. Solid solutions of the general formula $Na_{2x}Ca_{3x}Al_2O_6$ can arise from substitution of Ca^{2+} ions with Na+ ions. Higher degrees of substitution, greater than 1% Na_2O, can result in different structures (Taylor, 1990).

The C_3A compound may exist in four crystal structures (in the presence of alkalis) namely: cubic, orthorhombic, tetragonal and monoclinic (Regourd *et al.,* 1973; Maki, 1974a & b). According to Boikova *et al*. (1980), the C_3A phase with more than 3 wt % $Na_2O + K_2O$ appeared to be orthorhombic, while phases with fewer alkalis were cubic. Incorporation of impurities also affects the hydration rate. Boikova *et al.* (1977) determined the hydration rate of pure C_3A to be 60% at 10 minutes of which the hydration rate of the cubic solid solution was about 43% and that of the orthorhombic solid solution was about 37%. Bilanda *et al.* (1980) found that increase in Na_2O concentration in the absence of gypsum resulted in a decrease in the hydration rate, whilst the converse was true in the presence of gypsum.

A gel-like product at the C_3A surface is formed. This gel is the first hydration product of C_3A in the absence of calcium sulphate. It then changes into hexagonal crystals of the C_2AH_8 and C_4AH_{19} phases, and additional precipitates are formed from the liquid phase. These hexagonal phases act as a hydration barrier and therefore slow down further hydration of C_3A. These phases then convert to a thermodynamically stable cubic phase, C_3AH_6. Hydration proceeds again at a fairly higher rate since the diffusion barrier is disrupted (Vikan, 2005). The overall hydration process may be written as follows:

$$2C_3A + 27H \rightarrow C_3AH_8 + C_4AH_9 \rightarrow 2C_3AH_6 + 15H \qquad 2\text{-}1$$

The extent of C_3A hydration in the initial stages is reduced remarkably in the presence of calcium sulphate. The main product of hydration is formed as needle-shaped crystals called ettringite (AFT) (Figure 2.4).

$$C_3A + 3CSH_2 + 26H = C_6AS_3H_{32} \qquad 2\text{-}2$$

There may be an imbalance between the C_3A reaction rate and the calcium sulphate dissolution rate; hence an insufficient supply of sulphate ions, leading to the formation of minor amounts of monosulphates, C_4ASH_{12} or C_4AH_{19}. As ettringite formation liberates a significant amount of heat, the hydration rate diminishes markedly after the initial fast reaction (Vikan, 2005).

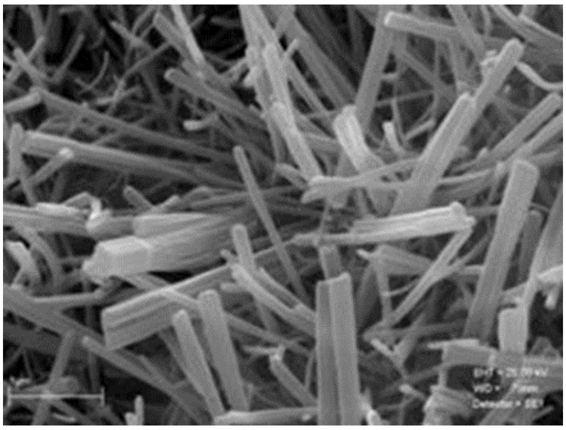

Figure 2-4;Precipitate of ettringite on C_3A surface (Adapted from arcvision.org, n.d)

According to Michaux *et al*. (1989), the duration of the dormant period is variable; increasing the quantity of gypsum in the starting paste results in an increase in the duration of the dormant period (Figure 2.5)

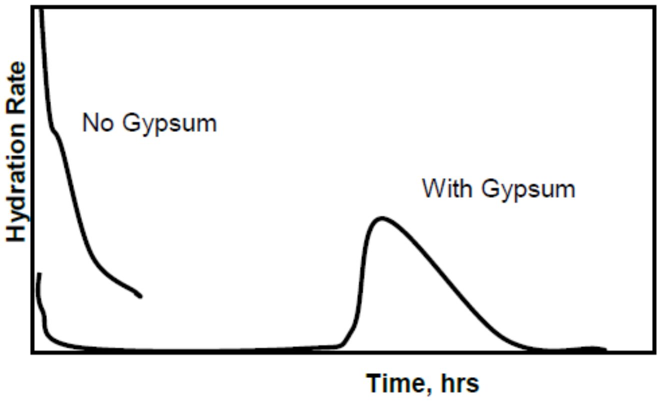

Figure 2-5:The hydration rate of C_3A and C_4AF, with and without gypsum (Adapted from Michaux *et al.,* 1989)

When all the gypsum has been consumed, a faster hydration in which the ettringite reacts with additional tricalcium aluminate occurs with a second heat release. The product of this reaction is calcium aluminate monosulphate hydrate (known as AFM). The reaction is expressed as per Equation 2.3:

$$CH_6AS_3H_{32} + 2C_3A + 4H \rightarrow 3C_4ASH_{12} \quad 2.3$$

Hexagonal calcium aluminate hydrate (C_4AH_{19}) starts to form as ettringite is used up; it may be present as separate crystals or as a solid solution with C_4ASH_{12}.

According to Vikan (2005), several theories have been suggested to expound the ambiguous dormant period associated with reduced hydration rate. The most widely adopted theories assume the build-up of an ettringite layer on the surface of C_3A and that precipitates on the C_3A surface since the presence of sulphates lowers its solubility. This layer slows down the hydration since it acts as a barrier. However, it has been argued that this barrier of ettringite crystals is less dense and cannot wholly cause hydration retardation. However, four alternative theories have also been suggested:

- A water-deficient hexagonal hydrate forms an impervious layer on the C_3A surface and is covered by ettringite. Incorporation of sulphates stabilises this hydrate;
- Adsorption of Ca^{2+} and SO_4^{2-} ions on the aluminate rich layer, thereby depleting the active dissolution sites, hence the rate of C_3A dissolution;
- Adsorption of SO_4^{2-} ions on the C_3A surface forming a barrier. On the contrary, C_3A dissolution is not slowed down by Na_2SO_4, implying that Ca^{2+} ions are required to form ettringite layers; and
- The C_3A hydration may diminish as a result of an amorphous layer which acts as an osmotic membrane at the C_3A surface.

Continual addition of $CaSO_4$ and conversion of ettringite to monosulphate results in the breakdown of the protective layer leading to termination of the dormant period. The conversion occurs by dissolution of both C_3A and ettringite, while precipitation of monosulphate occurs from the liquid phase in the matrix. Under comparable conditions, the products of the ferrite phase hydration resemble those formed by C_3A even though the rates are different and partial substitution of Al^{3+} by Fe^{3+} occurs in the product. The calcium aluminoferrite phase has variable composition ranging from about $C_4A_{1.4}F_{0.6}$ to $C_4A_{0.6}F_{1.4}$. The reactivity of ferrite increases with increase in A/F ratio.

Tricalcium Silicate / Dicalcium Silicate

During hydration reaction, both C_3S and C_2S react to form calcium-silicate-hydrate (C-S-H gel) and calcium hydroxide (CH), also called Portlandite. The C-S-H gel, comprising 70% of the mixture, is responsible for the strength development of the paste, while the CH raises the pH of the solution to between about 12.5 and 13 (Vikan *et al.,* 2007).According to Michaux *et al.* (1989), the reaction initially proceeds rigorously until the C-S-H impermeable gel accumulates around silicate particles, thus preventing further hydration of unhydrated C_3S and C_2S. This stage marks the beginning of the induction period, which ends with the gel eventually becoming permeable thereby allowing water to reach unreacted silicates. The hydration picks up again at that point. Since C_3S reacts faster than C_2S, it is therefore responsible for early strength development, while C_2S controls strength development at later stages.According to Vikan (2005) alite (C_3S) hydration occurs in four periods:

- Pre-induction period occurs in a few minutes just after water addition and is characterised by a great liberation of heat quantity.
- Induction (dormant) period is that in which the reaction rate decreases; hence the liberation of heat is reduced significantly, lasting for a few hours.
- Acceleration period is that in which the reaction rate increases rapidly to a maximum over a period of five to ten hours. Likewise, the concentration of $Ca(OH)_2$ in the solution rises to a maximum and begins to dwindle as $Ca(OH)_2$ precipitates. It has been proven that the initial set and the final setting time occur just after the start and end of this period, respectively.
- Deceleration period is that in which hydration slows gradually. Nevertheless, a notable diffusion-controlled reaction may persist for a long period after curing due to the excessive increase in thickness of the hydrate layer that develops on the surface of unhydrated cement grains.

The overall alite hydration reaction may be written as follows:

$$2C_3S + 7H = C_3S_2H_4 + 3CH \qquad 2.4$$

Hydration product

According to Grzeszczyk (1990), the degree of conversion of the clinker and the number of hydration products are determined by the clinker reactivity. In the suspension, especially in the liquid phase, there is a high concentration of ions such as Ca^{2+}, SO_4^{2+} and OH^-.

During hydration, each phase forms different products by disparate reaction mechanisms and at different rates. However, these reactions depend on each other, due to the nature of the particles and cement composition. The main hydration products are calcium silicate hydrate (C-S-H), calcium hydroxide (Portlandite), ettringite (AFT) and monosulfate (AFM) (Figure 2.6).

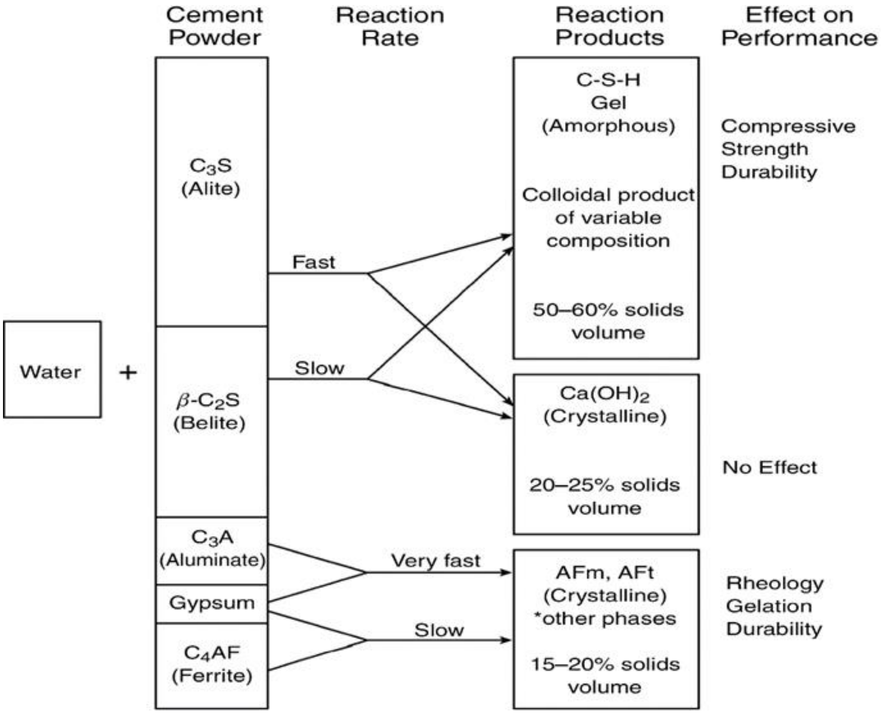

Figure 2-6:Hydration reaction of each phase (Adapted from Civil Scholar, n.d)

2.2.1 Effect of superplasticiser on hydration of cement paste

Various studies have determined a positive effect in the cement paste rheological properties when used with superplasticiser. El-Gamal *et al*. (2012) revealed that OPC used with superplasticiser had a better workability at lower water content as compared to cement paste without superplasticiser. This was explained as due to the effect of the superplasticiser coating the surface of particles, causing a higher dispersion and repulsion between particles. The flocs break up because of that repulsion and the release of trapped water improves both the workability and the water requirement of the cement paste. The addition of superplasticiser influences the volume of hydration and the distribution in the mixture, leading to alterations in particle size distribution, specific surface area and the number of particles, which are directly associated with the rheological behaviours of the cement pastes (Zingg *et al.,* 2008). The capacity of the superplasticiser to improve the workability of the cement is linked to its molecular weight: the smaller the molecular weight, the faster and the greater the adsorption onto the cement paste particles. The increase in fluidity of the cement paste after addition of superplasticiser leads to the reduction of required water/cement ratio. The SP has a great effect on the setting process of the cement paste.

Zhang *et al*. (2010b) define setting time as the stiffening of cement resulting from the interactions between cement particles during hydration. The initial set indicates the onset of loss of workability and marks the beginning of hardening. These researchers found that PLS, PCE and SNF-based superplasticisers retarded the hydration of cement, with the extent of reduction in hydration rate depending on both the dosage and the type of admixtures used. Similar observations have been reported by Puertas *et al*. (2005) who studied the impact of SP on the hydration reaction of cement paste. Superplasticisers slow down the hydration reaction, thereby affecting the morphology and microstructures of cement. For melamine and naphthalene-based SPs, the dispersion ability of SP in the suspension depends on factors such as C_3A and alkali content in the clinker, cement fineness, calcium sulphate, and the introduction of superplasticiser in the mixture. However, in the case of polycarboxylate SPs, it has been shown that calcium sulphate has a greater effect than C_3A on the fluidity of the paste.

Vikan *et al.* (2007) stated that the interaction between cement and SP was related to the SO_4^{2-} ions concentration in the suspension. They found that for the initial hydration, alkali sulphates (Na_2SO_4 or K_2SO_4) decreased the consumption of SP, which then made more SP available in the solution causing a low hydration rate and high flowability. The superplasticiser effect on the hydration kinetics of the cement paste has been studied by determining the value of the chemically-combined water for both pure and superplasticised cement paste. Results revealed a gradual increase in combined water throughout the various stages of hydration. The value of the combined water was slightly higher for the cement with superplasticiser due to the decrease in w/c ratio with the use of superplasticiser (El-Gamal *et al.,* 2012).

The cement paste properties are influenced by interactions between the particles and the medium. The superplasticiser, when added to the paste, gets adsorbed onto the particles; this in turn decreases flocculation and water entrapment in the flocks, significantly reducing the amount of water needed to achieve similar fluidity of the pastes.El-Gamal *et al.* (2012) found that the effectiveness of a superplasticiser additive depends on its level affinity with the cement and other mineral additives. Previous studies had shown that adding superplasticiser to non-blended cement led to an exponential or linear relationship between the adsorption of SP on cement particles and the SP dosage in cases of low concentration of the admixture. This period was followed by a plateau adsorption period where the addition of larger amounts of superplasticiser did not lead to further increase in consumption by the cement. The highest adsorption values obtained from previous work had shown the following results for CEM I: 14.28, 11.53 and 10.07 mg of superplasticiser/g of cement for lignosulfonate (PLS), melamine (SMF), and naphthalene (SNF) respectively. These results demonstrated the dependence of the rate of additive adsorption on the molecular weight of the superplasticiser.

The highest adsorption was achieved with the superplasticiser possessing the lowest molecular weight. Other studies have linked this trend with the radius of gyration of solid particles in the solution, concluding that a large radius of gyration leads to greater thickness; therefore, only a small dosage is required to achieve adsorption.

The preparation of cement paste involves a significant amount of solids. Therefore, in addition to particle/additive interactions, there are interactions such as particle-particle and particle-admixture-particle. It was found that the addition of superplasticiser to non-blended cement reduced the yield stress of the paste by hindering inter-flock aggregation (El-Gamal *et al.,* 2012). Another observation from the experiment carried out by Burgos-Montes et al. (2012) showed that PCE-SPs were more effective than SNF-SPs. In fact, to achieve the same results (in terms of yield stress values), a double amount in dosage of SNF was needed as compared to the concentration of PCE type SP. A very small amount of PCE was found to be able to reduce the cement paste yield stress by 90%. Research conducted by Schwartzentruber *et al.* (2006) concerning the effect of using both superplasticiser and viscosity enhancing agents found that when the superplasticiser dosage was used at saturation level, the VEA had very little influence on the rheological properties of the mixture.

2.2.2 Effect of limestone on the hydration of cement paste

Limestone finds its use in self-compacting concrete (SCC) as filler added in amounts ranging from 200 to 300 kg per m^3 of concrete. Self-compacting concrete is a relatively new developed material which differs from the traditional vibrated cement in terms of flow behaviour. A fundamental approach involving the flow properties of materials was thus used during the course of this research to gain insight into the effect of limestone on cement hydration.

Although limestone is stable, it is reported to participate in the cement hydration reactions (De Schutter, 2011). The presence of limestone in cement paste influences the hydration products formed. Lothenbach *et al*. (2008) showed through thermodynamic calculations and experimental observations that monocarbonate is more stable than monosulfate in the presence of limestone, in agreement with De Schutter (2011) who reported that the monosulfate converts to monocarbonate in the presence of limestone since the monocarbonate is more stable. Matschei *et al.* (2007) came to the same conclusion using thermodynamic modelling and solubility data. The monocarbonate makes ettringite more stable as the water and calcium hydroxide reacts with forming crystalline Ettringite (Celik *et al.,* 2015). The information about ettringite formation is still under debate. Tsivilis *et al.* (1998) and Kakali *et al.* (2003) found that limestone retards the formation of ettringite. However other researchers have produced different results. For instance, Ingram *et al.* (1990) found that limestone does not have any influence on the rate of ettringite formation. Ramachandran and Zhang (1988) stated that limestone accelerates the formation of ettringite.

Other studies (e.g. Voglis *et al.,* 2005) focussing on the transformation of ettringite to monosulfate in the presence of limestone observed that limestone retards the transformation. Recent investigations conducted by De Schutter (2011) concluded that limestone accelerates the rate of hydration of Portland cement. The researcher postulated that this might be due to the increased nucleation possibilities induced by the presence of limestone filler. The induction period is then shortened and the hydration reaction is accelerated in comparison with the case of cement without limestone. Figure 2.7 summarises the findings of De Schutter (2011) where the presence of limestone significantly reduces the hydration time.

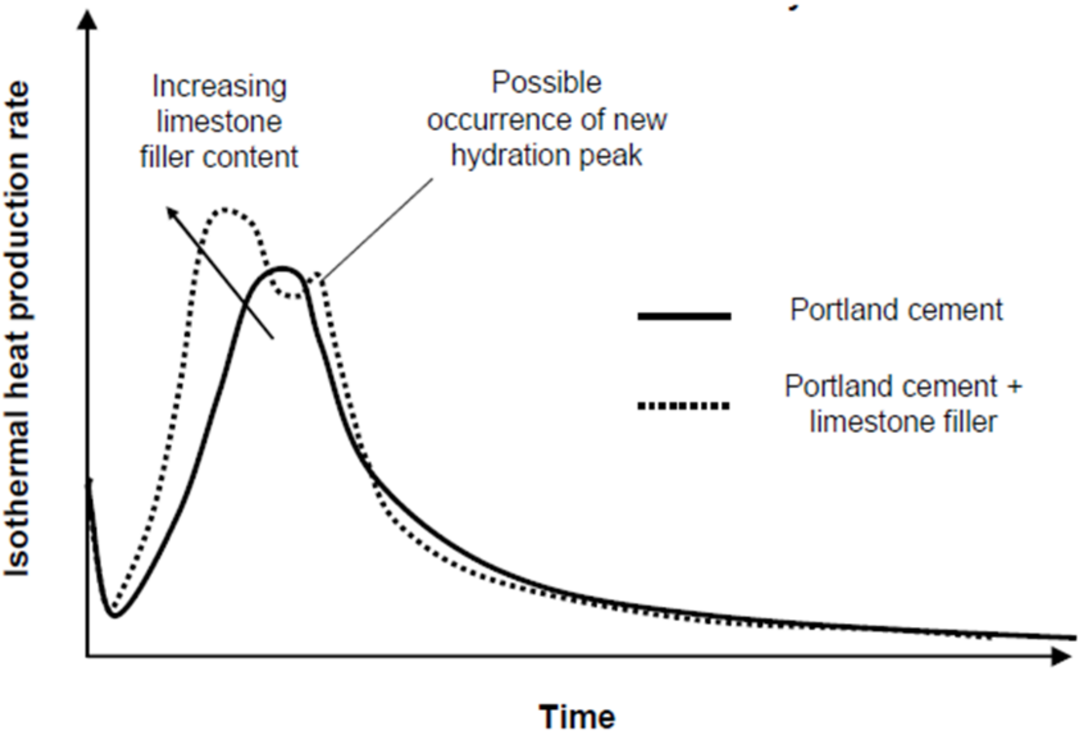

Figure 2-7: Effect of limestone on cement hydration(De Schutter, 2011)

This finding of De Schutter (2011) supported the view of Hooton *et al.* (2007) and Turker and Erdoğdu (2000) by specifying that limestone only increases the hydration rate in the early stages of hydration and has no effect in the later stage. Limestone in this stage does not affect the quantity of portlandite (CH) formed.According to Hooton *et al.* (2007), the fineness of limestone could possibly influence the hydration rate by increasing the fineness of the cement paste; therefore it might be difficult to differentiate between the effect of limestone content and the fineness of the materials.An extensive review on the influence of various mineral admixtures on cement paste was done by Hawkins *et al.* (2003) who considered different mixes, investigating their effect on the hydration of blended cement paste using thermodynamic technics.

Chemical effect

The reaction of limestone in the form of pure compound or as ground limestone with Type II cement was studied by Klemm and Adams (1990) using hydration times as long as one year. They found that kinetics of monocarboaluminate formation were slower than that of ettringite. A significant amount of limestone (around 85%) remained unreacted after 129 days. It was further concluded that Type II cement acted as an inert dilutant. From a thermodynamic point of view, they postulated that the stability of the reaction phase decreased in the following order: ettringite > monocarboaluminate > monosulfoaluminate.Barker and Cory (1991) found that the amount of monocarbonate increased with the amount of limestone added for cements with a higher C_3A content.Bensted (1980) discovered that C_3A reacts with limestone forming tricarbonate and monocarbonate in the absence of gypsum. Ettringite was found to be formed during early stages of hydration while monosulfate formed at later stages. However, ettringite is more stable than tricarbonate at room temperatures; hence, it does not exist in cement hydration. He further concluded that the substitution of limestone for 25-50% gypsum had no effect on cement hydration.

Physical effect

It is generally accepted in the literature that the effect of limestone on cement hydration is dominantly chemical. However, some researchers argue that limestone also has physical effects on cement hydration. Sprung and Siebel (1991), for example, argued that limestone fillers improve particle packing as well as promoting nucleation of hydration products. It has been found that even when replacing the clinker, limestone improves physical properties of cement. For instance, after grinding process, Campiteli and Florindo (1990) found coarse particles within the inter-ground cement from clinker without limestone, whereas with the addition of limestone to the clinker, finer fractions were found within the ground cement. The implication of these findings is that when limestone replaces a clinker during cement manufacture, the specific surface area of the final product is affected.

Heat evolution

The hydration of the cement is an exothermic process. Hooton (1990) asserts that the heat involved during hydration was not consistent. Barker and Matthews (1993) found that the maximum heat rate is generally reduced when limestone is used. However, the influence of limestone on the time at which the maximum heat rate occurs is influenced by the limestone cement preparation method employed. Using blending as a preparation method has no effect or retards, while preparation by inter-grinding accelerates the timing of the peak heat rate. Livesey (1991a & b) reported that the rate and total heat of hydration decreased with increasing limestone content.Contrarily, Ramachandran and Zhang (1988) reported that increasing the limestone increased the total heat evolved. Furthermore, it was reported that the magnitude of heat produced was higher with increasing limestone content, particularly for C_3S paste in the first 24 hours (Ramachandran, 1988). Cements with 5% of limestone or without it produced equal hydration heats, but for higher fineness cements (Vuk *et al*., 2001). From the preceding discussion, Hawkins *et al.* (2003) made clear that there are contradictions on the effect of limestone on cement hydration.

2.2.3 Interactions between limestone and superplasticisers

Moratti *et al.* (2012), using limestone blended cement, found that short side chain polycarboxylates significantly retarded the hydration reaction. Likewise, Mikanovic and Jolicoeur (2008) investigated the effect of SPs on the rheology and dynamic stability of both cement and limestone pastes, discovering that the dispersing capacity of SNF and PCE type SPs were similar in a pure limestone paste. It was found that the addition of $Ca(OH)_2$ to the limestone paste increased the dispersion capacity of the PCE type SPs at a pH of 12.5. This observation was attributed to both steric and flocculation effects.

Bizzozero and Scrivener (2015) used both experiments and thermodynamic simulation to show that the reaction of limestone depended on the relative quantities of aluminate and sulphate. Two scenarios were noted in the calcium aluminate cement–calcium sulphate system. Firstly, all the gypsum might react: calcium aluminate reacts with carbonate ions from the limestone to form hemicarboaluminate and monocarboaluminate. The ettringite formed is conserved instead of reacting with C_3A to form calcium aluminate monosulfoaluminate. Secondly, there might be excess of gypsum: all the C_3A available in the cement reacts with SO_4^{2-} ions present in the suspension to form ettringite and aluminium hydroxide. In this case, limestone acts as filler.

For systems with the lowest calcium sulphate content, the proportion of limestone reacting is 4 g for every 100 g anhydrous solid. Such a small quantity of limestone has significant impact on these systems, especially their mineralogy. Their strengths are similar or even higher than in systems free from limestone. For systems with higher sulphate content, more ettringite is formed, resulting in higher compressive strengths. The undesirable effect is that such systems are vulnerable to uncontrollable expansion culminating in complete destruction of the material.

2.2.4 Factors affecting hydration

According to Zingg *et al*. (2009), during early hydration, various factors affect and impact the workability and the flowability of the cement paste. Factors such as C_3A content and soluble sulphates amount had a direct influence on workability, whereas particle size distribution, packing density and surface area of particles were associated with the flowability of the paste.

Surface area

Several researchers such as Nachbaur *et al.* (2001) have shown that the strength of the attractive forces in a cement paste was due to physical forces. Physical forces among particles surfaces are responsible for most of the physical strength, while chemical forces contribute only to a certain extent. The modulus was shown to depend mainly on the geometry of aggregates of particles rather than inter-particle forces. Therefore, it was possible to witness an increase in modulus without any change in inter-particle forces (Nachbaur *et al.,* 2001).Surface area plays an important role when superplasticiser is added to the mixture. Vikan *et al.* (2007) have shown that the relatively high surface area of C_3A increases the superplasticiser saturation dosage and hydration rate. This can be explained by the higher amount of superplasticiser absorbed on the surface of the cement.

Water-cement ratio

Water content of the cement paste has always been considered one of the key factors influencing various rheological properties and also necessitating optimisation, as there is a trend towards the reduction of water usage due to environmental concerns. Several studies have focused on how water/cement (w/c) ratio could effect on the cement paste hydration (Kirby & Biernacki, 2012). In their previous research, Kirby and Biernacki (2012) linked the w/c ratio to the onset of nucleation, finding that the onset of nucleation was directly proportional to the w/c ratio. The addition of water was shown to aggressively accelerate the hydration rate when the water/cement ratio was increased from 0.3 to 0.8. Above a w/c ratio of 0.8, the nucleation rate is inhibited; however, the rate of reaction after the onset of nucleation remains unaffected. The reasons for this phenomenon remain unclear in the literature, as the addition of water should be expected to lead to further delay in nucleation rate by increasing the saturation level required above which nucleation is possible. However Kirby and Biernaki (2012) postulated that the increased rate of nucleation might be due to the additional water freeing more available space for the nucleation.

The rate of nucleation above a w/c ratio of 0.8 was found to be delayed due to excess of water in the admixture and the increase in saturation level. However, the rate of hydration after nucleation remained unchanged; this suggests that the special constraints or the levels of dispersion of the particles are not altered (Kirby & Biernacki, 2012). At a water/cement ratio less than 0.36-0.38, there is not sufficient water to lead to full hydration, leaving some cement unhydrated, which necessitates the replacement of some of the cement with limestone (Hooton *et al*., 2007). Water-cement ratio affects the hydration kinetics after the middle stage of hydration; however, it has been shown to have an insignificant effect in the early stages of hydration. The water/cement ratio also influences the ultimate degree of hydration.

In contrast, Neville (1996) (as cited by Amen, 2011) stated that a water/cement ratio of only 0.23 is sufficient for complete hydration of Portland cement compounds.The author(s) modified the statement, ‘But in practice, due to various factors slowing the water diffusion, the full hydration (Lin, 2006) of the whole cement paste is rarely achieved.’

Lin (2006) found that the degree of hydration is given by Equation 2.5:

$$\alpha_u = \frac{1.031\,{}^{w}/_{c}}{0.194 + {}^{w}/_{c}} \leq 1.0 \qquad 2.5$$

This equation, although providing a good approximation of the hydration level, does not take into account the cement fineness or the curing temperature, and therefore may not adequately describe the hydration of the cement (Lin, 2006). In other studies, the impact of water/cement ratio in cement paste containing limestone was investigated, with results showing that the degree of hydration was remarkably higher for a high water/cement ratio (> 30 %), but at a low water/cement ratio of approximately 0.30, the difference in hydration was not noticeable (Hooton *et al*., 2007). Bentz (2006), though, found an opposite trend where the rate of hydration increased significantly at low w/c ratio and was negligible when higher w/c ratios (> 0.435) were used.

Fineness of the cement

The fineness of the cement has an influence on the ultimate degree of hydration as well as the hydration αu. Previous studies have determined that the finer the particles, the higher the ultimate degree of hydration (α_u). It has also been established that the effect of the fineness of the cement on the hydration decreased at low water/cement ratio. A finer cement particle provides a larger surface area which leads to a higher hydration rate (Lin, 2006).

Aiqin *et al.* (1997) determined that the particle size distribution (PSD) significantly affects the hydration kinetics as well as the packing density of the cement paste. The packing density obviously affects the porosity of the paste. These researchers discovered that a narrow PSD translates to improved hydration kinetics and a wide PSD is associated with a higher packing density. Optimum kinetics and packing density required a ratio of 0.3 between the coarse and fine particles. Their results were confirmed by Celik (2009) who found that the PSD had an effect on water demand, hydration and settling.

Curing temperature

The curing temperature has a higher impact on the hydration of the cement paste. In fact, the reaction rate increases with increasing temperature. Lin (2006) reported a relationship between the volume of the hydration products and the curing temperature of cement paste.
Equation 2.6 was established as the ratio between the volume of the hydration products and the reacted cement at temperature *T* (Lin, 2006):

$$v(T) = \frac{Volume\ of\ hydration\ products\ at\ T}{Volume\ of\ reacted\ cement\ at\ T} \tag{2.6}$$

$$v(T) = v_{293} exp[-28 \times 10^{-6} (T - 293)^2] \tag{2.7}$$

According to Lin (2006), there is still limited understanding of the effect of curing temperature on different properties of cementitious materials.

2.2.5 Different techniques to follow the hydration process of cement paste

Different techniques, proven to be effective in determining the phase composition of clinkers, are used to study the hydration and the microstructure of cement paste, including the following:

- XRD (X-ray diffraction): This is a qualitative method in which intensities may be used to estimate amounts of phases with great uncertainties in determining quantities. The device makes use of X-rays generated from Cu Ka radiation with Ni filter. This technique should primarily be used for detecting retardation or acceleration trends in the hydration reactions of cement pastes. In this context, a delayed or earlier onset of increasing or decreasing net peak heights will be referred to as retardation or acceleration of any phase, respectively (Danner *et al.,* 2016).
- TGA (thermogravimetry): According to Jo*et al.* (2015), TGA is conducted by heating a sample at a controlled rate and determining the dynamic weight loss from the heated sample. This analysis is done in an inert environment, such as a nitrogen atmosphere, to avoid carbonation and any kind of contamination. Better identification of the changes can be achieved by calculating the corresponding derivative thermogravimetric (DTG) curve, because the DTG curve has notable inflexion points,

plateaus and features that are not obvious in the TGA curves and can be used to better track all different processes. The principle of this method lies in tracing the derivative curve, and measuring the weight loss corresponding to the beginning and the end of the derivative peak. The weight lost can be easily computed by integrating the peak of the derived curve. According to Kocaba (2009), the amount of portlandite and calcite can be computed using the first derivative curve as an alternative method.

- SEM (scanning electron microscopy): According to Kocaba (2009), the images obtained from the scanning electron microscope (SEM) are indispensable in investigating the microstructure of materials. These have been used extensively to conduct both quantitative and qualitative studies of the evolution of the microstructure of cementitious materials during their hydration.The contrast between areas with different chemical compositions can be detected using backscattered electrons imaging: the bigger the difference between the average atomic numbers of the various regions, the more easily the regions can be observed. Heavier sample atoms result in greater backscattering of the electrons, hence brighter images. The average atomic numbers of the considered phase or material, or its internal micro-porosity, determine the yield, energy spectrum and depth of escape of backscattered electrons. Phase discrimination becomes possible as a result of the specific contrast and brightness on the screen. In the case of cementitious materials, the depth of interaction volume from which BSEs are detected is about 0.05-0.2 μm across, depending on the acceleration voltage (Jo *et al.*, 2015).
- Isothermal calorimetry: The hydration process can be followed using calorimetry. The kinetics of the reaction can be studied since the reaction is highly exothermic. The advantage of this technique is that it allows the hydration process to be followed in-situ, continuously, at realistic water/cement ratios, without the need for drying and by following the overall rate of heat evolution; it aims to give an indication of the overall rate of reaction (Kocaba, 2009).The major drawback, though, is that only the overall heat evolution can be measured which constitutes the heat evolved by all the reactions occurring at any particular time. Despite having high rates of reaction, the rate of heat output could be negligible if exothermic and endothermic reactions occur simultaneously. As such, calorimetry can only be used as a global measure of the degree of hydration.
- Rheometry: Rheometry is defined as a set of techniques that can be used individually or simultaneously to acquire rheological data of a certain material. Different rheological parameters are measured either to study the flow properties or the structure development of the cement paste during hydration process. It is agreed that

rheological properties of cement paste are influenced by its intrinsic structure. From the initial contact with water the paste goes through different rheological states comprised between viscous state and solid state due to the presence of colloidal attractive forces and nucleation and growth of some hydrate at contact points within the suspension. The storage modulus in different conditions of strain, strain rate can be measure to provide information about these observed transformations undergone by cement during hydration (Bellotto, 2013). The later technique was used in this work. More details about rheology and rheometry methods were illustrated in the next sections.

2.3 Rheology

The term rheology comes from the Greek rheos which means the river, flowing, streaming; and the suffix logy refers to study.Rheology has therefore been defined as the science that studies the deformation of solids and flow of fluids (Malkin, 1994; De Larrard *et al.,* 1994). Mezger (2002) suggests that the relationship between stress, strain, strain rate and time should be considered in order to characterise the flow behaviour of materials.There are two extremes under which all materials can be viewed: ideal viscous liquids and ideal elastic solids (Mezger, 2002). In reality, many materials are between these two extremes, referred to viscoelastic materials as these materials have both elastic and viscous properties.

Rheology defines a specific material in this range based on its yield stress and viscosity. The yield stress of material is defined as the stress to be overcome to initiate the flow while the viscosity is referred as to the property of material to resist the flow (De Larrard *et al.,* 1994). This science has been used as a tool to define and characterise different types of material in different technological industries. For instance, the quality of paints is controlled based on their rheological parameters (Stokes *et al.,* 2005). The implementation of rheology in food industries has been done successfully by providing the means to design different food products based on their rheological properties (Barnes & Nguyen, 2001; De Krester *et al.,* 1997; Zhu *et al.,* 2001).The concrete industry has also been using rheology as a tool to study various properties of cementitious materials by relating them to their determined rheological parameters (Banfill, 2003).The determination of rheological parameters is thus critical when studying the behaviour of a given material. This is made possible by establishing rheological models based on the properties of the material under investigation.

2.3.1 Rheometry

Rheometry is defined as the techniques used to obtain rheological data. The correct acquisition of these requires sophisticated instrumentation, effective experimental procedures and a consistent analytical approach. There are two types of procedures and both can be done with the same instrument; the rheometer. The oscillatory mode is more convenient for viscoelastic materials while the rotational mode is more convenient for viscous materials (Mezger, 2002).

Rotational viscometer

The rotational viscometer consists of concentric bob and cup. The shear is achieved by the rotation of the concentric bob in the annular space containing a liquid, between a stationary cup and rotating cylinder. The shear stress is evaluated through the applied torque on one of the elements. There are various geometries used as attachments for rheometers such as concentric cylinders, cone and plate, and parallel disks (Figure 2.8). The main measured parameters are angular velocity and torque which are then converted to shear rate and shear stress using appropriate formulae (Chhabra & Richardson, 1999).

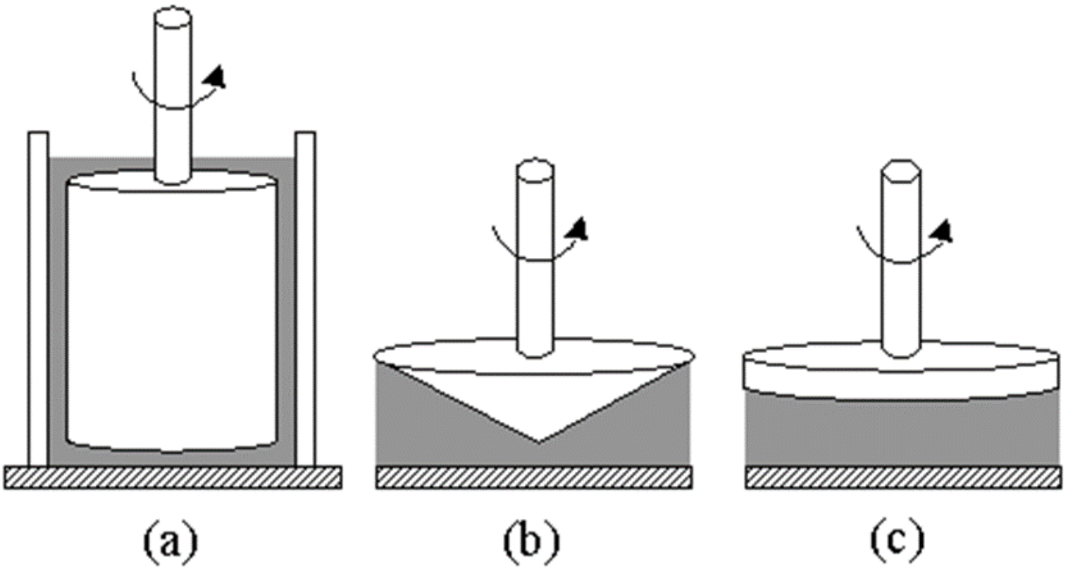

Figure 2-8:Different rheometer types: (a) the concentric cylinder type, (b) the cone disk, (c) parallel disk type (Adapted from Teachengineering, 2016)

Oscillatory viscometer

The essence of an oscillatory rheometer for dynamic mode measurements is to cause a sinusoidal shear deformation in the tested material and the response to the initiated stress is recorded. Oscillatory tests are used to investigate various viscoelastic materials which can range from low viscosity liquids to solids. The types of tests conducted in this way are known as dynamic mechanical analysis (Mezger, 2002).The oscillating system consists of two plates with the top plate oscillating by the use of a turning wheel with an eccentric push rod attached. As the wheel starts turning, the upper plate moves back and forth while the lower remains stationary, resulting in the shearing of the materials located between the plates. The following requirements must be met: the sample must fully adhere to the plates and not slide out during the operation; and secondly, the sample must be homogenously sheared and deformed between the two plates (Mezger, 2002).

Advantages of oscillatory testing are as follows:

- an increase in the measuring range;
- a non-destructive method;
- analysing the structural properties of a material; and
- monitoring all changes depending either on time or temperature.

Various techniques are used in rheometry to assess the rheological behaviour of fluids.

Amplitude sweep

Amplitude sweep, a technique carried out in oscillatory mode, consists of shearing the material under variant strains at a constant frequency (Figure 2-9). The viscoelastic response of the materials is determined by monitoring both its storage and loss moduli. The evolution of moduli within a material depends strongly on the applied stress frequency. Thus, the loss modulus increases at high frequencies until it reaches a maximum value; thereafter, it progressively decreases to its minimum value. Simultaneously, the storage modulus increases gradually until a roughly constant value is attained. At this point, the storage modulus displays little dependency on the frequency (Wyss *et al.,* 2007).

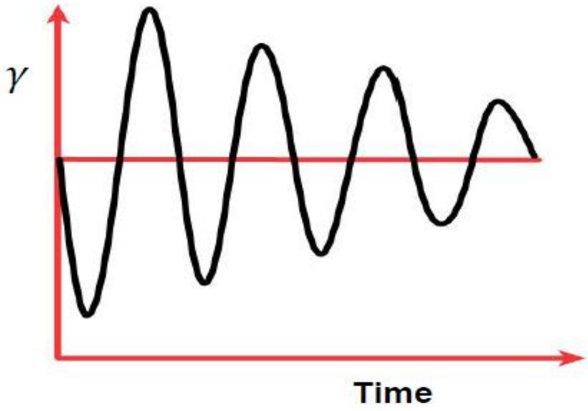

Figure 2-9:Amplitude sweep, constant frequency and variable strain (Adapted from Mon Tech, n.d)

Testing may use a controlled shear strain (where the strain amplitude is varied for a constant angular velocity) or controlled shear stress (where the stress amplitude is varied for a constant angular velocity) (Atomikateknik, 2011). Generally for industrial applications, the constant angular frequency is selected at a value of $10s^{-1}$ corresponding to a frequency of approximately 1.6 Hz (Mezger, 2002). However, amplitude sweep is not suitable for samples in a state of rest, because the value of a frequency of about 1.6 Hz does not represent a material at rest. When testing materials at rest, very low frequencies need to be used (Mezger, 2002). In the linear viscoelastic behaviour region (LVR) at small amplitudes, both the storage and complex modulus show a constant plateau value. In this region, the pre-set and measured parameters are always proportional, and their relationship is characterised by a straight line on the corresponding graph (Atomikateknik, 2011). This method allows for determining different states of a material:

Gel character

In a case where the elastic behaviour dominates the viscous behaviour, there is a certain rigidity of materials. This can be observed in dispersions with low viscosity at high shear rates, being rigid gel-like structures in the liner viscoelastic range (LVR). Therefore these materials have a certain form-stability (sometimes these kinds of samples are called paste type materials) (Atomikateknik, 2011).

Liquid character

In this case, the viscous behaviour of the mixture dominates the elastic behaviour. The material possesses a liquid character in the LVR. These types of materials do not remain stable; they flow, although sometimes at low velocity. These fluids are capable of forming a level surface at rest. An example of this are polymer melts (Atomikateknik, 2011).

Frequency sweep

This technique is used as well in oscillatory mode where the frequency is varied while the amplitude is maintained constant. In most literature, this is referred to as dynamic oscillation (Thermo, n.d). The frequency test shows the material's "fingerprint" profile. The frequency sweep test allows classification of materials into three rheological behaviours: viscoelastic solid, gel and viscoelastic liquid (Atomikateknik, 2011). The time dependency of the material can also be assessed with this technique. Rapid movements are used to determine short-term behaviour of materials while slow movements are used to determine their long-term behaviour. The sample is subjected to oscillations with small deformations over a certain range of frequencies to investigate the response of the material to the deformations (Rheology School, 2013).

The number of oscillations per unit time can be specified in two ways: as frequency f or as angular velocity ω. However lately angular velocity ω has been increasingly used instead of frequency f and ω is often referred to as angular frequency (Malkin & Isayev, 2006).

The test setting can be done by either controlling the shear strain while varying the shear rate, or by controlling the shear stress while varying the shear rate. Before performing the frequency sweep test, the LVR range of the material must be determined. For that reason the amplitude sweep should always be performed prior to the frequency test. Thereafter, the conditions for the frequency test can be established (Mezger, 2002).

The oscillatory frequency sweep technique allows one to identify and investigate the microstructure within a given material. Figure 2.10 demonstrates how the variation of frequency within a certain range can help distinguish materials with 'relax-able' structures from those with permanent elastic structures, an important and useful technique when dealing with flow behaviour in thickening systems.

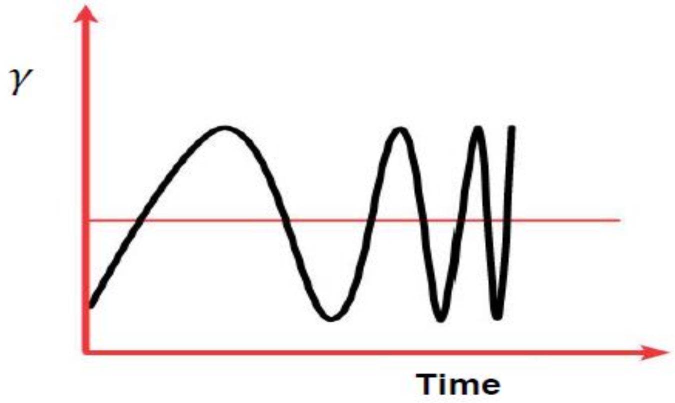

Figure 2-10:Frequency sweep, constant strain and variable frequency
(Adapted from Mon Tech, n.d)

Time sweep

In this type of oscillatory test, the material is sheared under a constant strain and frequency and the response in terms of complex modulus is observed over time. The constant amplitude value is less than the critical strain of the sample. This test is used for analysing the time-dependency behaviour of samples whose properties change with time. The change in microstructure due to the chemical reaction within the material can be determined by monitoring the evolution of moduli over time (Malkin & Isayev, 2006).

Gel point and gel time

The time-dependent hardening curve can generally be described as having two regions, viz:

- sol or liquid state: this is the interval in which *G">G'*
- gel or solid state: this is the interval in which *G"<G'*

The gel time for the cure behaviour of the material is the time at which tanδ is maximum while the gel point is the time at which *G' = G".*

If a curing experiment is conducted isothermally at a temperature at which the uncured resin exists in liquid phase, the sample forms branched molecules and gels with a sharp increase in viscosity to the extent that a glassy solid may be formed. In this scenario, the tan*δ* curve is characterised by two peaks: the first one being gelation and the second one being vitrification. If only one peak is observed, however, it can be attributed to either of the processes.It is in this context that oscillatory tests have an advantage over rotational tests. Rotational tests do not capture additional information about the structural character. As alluded to earlier, oscillatory tests give information regarding the sol and the gel state. Furthermore, since oscillatory tests are conducted in the linear viscoelastic range, the experimenter has the upper hand in maintaining test conditions within suitable limits to conduct a non-destructive test on the structure of the sample (Mezger, 2002).

2.3.2 Rheological parameters

Storage modulus

The storage modulus represented by *G'* measures the deformation energy contained in the material at the beginning of the shear process. After the applied stress is removed, the energy is still available to act as compensation for the deformation and to recover the initial shape, fully or partially. In cases where energy-storing materials remain unaltered after the load has been removed, they can be said to display reversible deformation behaviour. The storage modulus thus represents the elastic behaviour of a material. The storage modulus can be expressed by Equation 2.8:

$$G' = \left({}^{\tau}/_{\gamma}\right) \cos\delta \tag{2.8}$$

Loss modulus

The loss modulus *G"* measures the deformation energy lost in the process and which will not be recovered at the end. The energy is either used up in the process with changes of structures or lost to the surroundings. Any energy-losing material which does not recover its original shape is considered to display irreversible deformation behaviour. Therefore *G"* represents the viscous behaviour of a material (Malkin & Isayev, 2006).
The loss modulus is given by the following equation:

$$G'' = \left({}^{\tau}/_{\gamma}\right) \sin\delta \tag{2.9}$$

Loss factor

The loss factor, the quotient of the loss and the storage modulus, helps determine the ratio of the viscous to the elastic portion of the deformation. This is represented by this equation:

$$\tan\delta = {}^{G'}/_{G''} \tag{2.10}$$

Table 2.1 specifies the state of the materials in terms of their loss factor. For ideal elastic materials, δ= 0, therefore tanδ=0, as *G'* fully dominates the material behaviour. On the other hand, in the case of an ideal viscous material, δ= 90^{o}, therefore tanδ=∞, in this case

*G"*completely dominates the behaviour of the material. However for *δ*= 45°, there is a perfect balance between the viscous *G"* and the elastic *G'* forces (Mezger, 2002).

Complex modulus

The rheological behaviour of all viscoelastic materials has two components: the viscous portion represented by the loss modulus *G"* and the elastic portion represented by the storage modulus *G'*. These two portions are represented in vectorial form along the x and y axis, as illustrated in Figure 2.11. The length of each component represents the corresponding value. Their resultant represents a new parameter called the complex modulus *G**. The complex modulus is therefore the resultant vector of both *G'* and *G"* vectors. *G** reflects the complete viscoelastic behaviour of a material. *G** can be calculated from the values of the loss and storage moduli (Malkin & Isayev, 2006). When the loss modulus *(G")* equals zero, the material is completely elastic (ideal solid) and *G* = G',* but when the storage modulus *(G')* equals zero, the material is ideal liquid and *G* = G"* (Schultz & Struble, 1993).

The complex modulus presents the stiffness of a material; the higher the modulus the tougher the material. The most common type of measurement used for this are the amplitude or strain sweep and the frequency sweep types of oscillatory tests (Wyss *et al.,* 2007).
The complex modulus can be expressed by Equation 2.11:

$$G^* = \sqrt{G'^2 - G''^2} \qquad 2.11$$

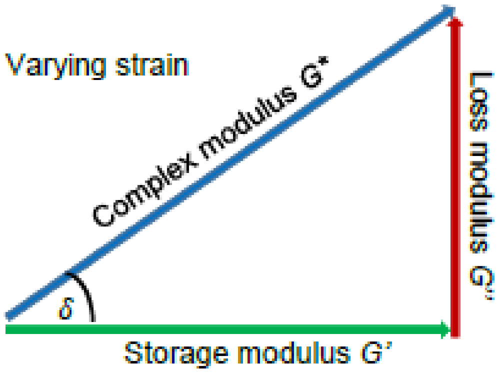

Figure 2-11:Complex modulus and loss factor (Adapted from Chaplin, 2012)

Table 2-1:Analysis of viscoelastic behaviour of material

(Adapted from Mezger, 2002)

Ideal viscous flow behaviour δ= 900 or $\tan\delta = \infty$	Behaviour of a viscoelastic liquid *G" > G'*	VE behaviour with a 50/50 ratio of viscous/elastic portion $\delta = 45^\circ$ or *G" = G'*	Behaviour of a viscoelastic solid *G' > G"*	Ideal elastic deformation behaviour $\delta = 0^\circ$ or *tan* δ *= 0*

2.3.3 Rheology of cement paste

According to Banfill (2006), cement paste is a viscoelastic material and this viscoelasticity of cement was found to change during the process of hydration. All the rheological investigations on cement paste were carried out using paste concentration, cement composition and fineness, aluminous cement and chemical admixtures, and considered the effects of age and temperature. Significant findings were that cement paste was shown to have a yield stress and its apparent viscosity was shown to decrease with increasing shear. Furthermore, the value of the viscosity and yield stress finally reaches equilibrium when the time of mixing is increased, a finding which has been confirmed by previous experiments (Banfill, 2003).

The addition of superplasticiser has been shown to affect rheological properties of cement paste. Previous work has demonstrated that the addition of superplasticiser leads to a decrease in viscosity of the cement paste. However, this decrease is highly dependent on the type of superplasticiser used (Papo *et al.,* 2004). According to Zingg (2009), the introduction of superplasticisers helps with the preparation of self-compacting concretes owing to the influence of superplasticisers on concrete flow properties. At higher dosage, some SP types can lead to bleeding phenomenon.

Rubio-Hernandez *et al.* (2013), using self-compacting concrete paste with limestone, reported that the addition of even a small amount of limestone led to a decrease in yield stress, while a higher concentration caused an increase in yield stress. This observation was because at low limestone concentration, there are only a few limestone particles in the mixture which do not interact with superplasticisers. Due to the smaller size of the limestone particles compared to cement particles, they occupy the interstices between various cement particles, causing a decrease in the microstructure.

This is consistent with the findings of Knop and Peled (2016) who observed that cement with finer limestone particles had a lower packing density, resulting in longer setting times, since the high surface area increased the hydration rate. However, larger limestone particles exhibited a higher packing density and reduced setting times and the lower surface area led to a reduced hydration rate.

Different method for acquisition of rheological parameters of cement paste

Various methods have been identified in the literature for measuring the viscoelastic behaviour of cement paste based on the dynamic rheology theory, as discussed in detail by Sun *et al*. (2005). Some of these methods are as follows:

Ultrasonic shear wave measurement methods

These were used by Sun *et al.* (2005) to determine the wave reflection coefficient by using a fused quartz plate with a given thickness of materials. Two transducers with a constant central frequency combined with the quartz plate. The device is connected to a computer via pulsars. The properties of viscoelastic materials in complex format can be determined by using the value of the reflection coefficient and appropriate mathematical correlations.

Strain sweep and frequency sweep rheometric methods

This two-step method is used to define the linear viscoelastic region (LVR) range of materials (Sun *et al.*, 2005). First, an amplitude or strain sweep is used to determine the value of the critical strain. A low frequency is used during strain with a determined water/cement ratio. The critical strain is determined at the value where the shear moduli start to decrease. Then, the frequency sweep is used to determine the critical value of the frequency. The value of the frequency is determined at the value at which the shear modulus starts to reduce.

Oscillatory rheometric (OR) methods

The OR-method has been used significantly in recent decades in various research using a strain control rheometer. This consists of co-axial cylinders with diameters of various sizes. A gap of a given value between the outer and inner cylinder is set. Hand mixing is often used in this method to prepare the samples before being transferred to the rheometer. Hand mixing is followed by pre-shearing in the rheometer. The cement is then allowed to rest in order to achieve structural equilibrium. During the oscillatory testing, the strain-control mode is used (Sun *et al.*, 2005).

Step rheometric methods

From previous work, this method, similar to the oscillatory method, was used to investigate the evolution of viscosity. The cement is transferred to the rheometer and a high shear rate is applied to bring the particles to a stress status that can be reproduced in several measurements, after the cement has been allowed to settle until the cement particles reach equilibrium. Segmented shear tests were thereafter used with a progressive decrease of shear rate with a uniform step. For each shear strain, the shear stress is measured. The curve of the rate of stress-strain can be used to determine the viscosity of the materials by determining the slope of the curve (Sun *et al.,* 2005).

For rheological methods, it is imperative that the researcher chooses the optimum measurement parameters that mitigate errors, both random and systematic, during the tests. Factors that impact the rheological properties of cement paste are as follows:

- sample preparation;
- operating temperature; and
- mode.

Sample preparation

The sample to be analysed must be mixed well to produce a homogeneous sample free of agglomerates, lumps or clusters (Yang & Jennings, 1995). Mixing can be achieved manually (Nachbaur *et al.*, 2001) or mechanically using a mixer. The effect of different techniques on the rheology of cement paste was investigated by Williams *et al.* (1999) who reported that the pre-shearing of a hand-mixed paste at a certain shear rate resulted in a sample with structural similarity to the one prepared in a mixer.

Operating temperature

Fernàndez-Altable and Casanova (2006) recommended that experiments be conducted at temperatures in the range between 5 to 25°C where the rheological behaviours of cement paste are not temperature-dependent.

Mode

There is still much debate on what mode should be used in studying the evolution of cement paste microstructure; however, most researchers have used the shear mode rheology to study the evolution of cement paste microstructure (Nehdi & Rahman, 2004; Vikan *et al*., 2007; Fernàndez –Altable & Casanova, 2006). Researchers have proven beyond doubt that the shear mode does not always affect the process of cement hydration. They found that the rheological behaviours of the cement paste are related to both chemical and physical properties of cement.Dynamic mode has successfully been used to investigate the properties of cement from mixing to setting. The non-destructive measurements (i.e. without destroying cement structure) are mostly used for this purpose within the linear viscoelastic region (LVR). However, this technique is still facing some uncertainties, rendering it difficult to reach proper conclusions regarding the evolution of the paste and the mechanical and rheological properties changes that occur. This problem was previously highlighted by Schultz and Struble (1993).

2.3.4 Rheology and hydration process

In an earlier work investigating modulus in the different stages of cement hydration, the storage modulus was used instead of complex modulus as the loss modulus was negligible (Bellotto, 2013). It was found that as the hydration reaction proceeds, the elastic modulus increases corresponding to the hardening of the cement paste.The elasticity of the paste develops from the initial contact with water, possibly due to the attractive inter-particle forces. One of the main causes of the attractive forces between particles in the precipitating hydrates is the high surface charge density of the C-S-H gel.Another cause of hardening of the cement is the steady increase in the storage modulus during the dormant period. This continuous increase has been associated with the formation of C-S-H and the strengthening of the inter-particle bonds (Bellotto, 2013).

As cement begins to hydrate, the increase in the concentration of ions affect the surface charge of the particles which then increases the attraction between particles. This is one of the reasons for the increase in yield stress (Lei & Struble, 1997). The nucleation of C-S-H in the dissolution stage changes the particle-particle interactions into a rigid structure with a network of C-S-H bridges. Figure 2.13 explicitly shows the structural development of cement paste. Cement particles get dispersed at the end of mixing. The nucleation of particles at pseudo-points of contact within a few seconds leads to flocculation of particles, thus transitioning from discrete particle system into a rigid particle system with an ability to overcome stress. In essence, C-S-H nucleation changes particle-particle interaction to C-S-H bridges and this is associated with a microscopic increase in the elastic modulus. After several tens of seconds, C-S-H bridges are the predominant mode of particle interaction (Figure 2.12) and the improvement in rigidity is a function of the number and size of C-S-H bridges created between particles.

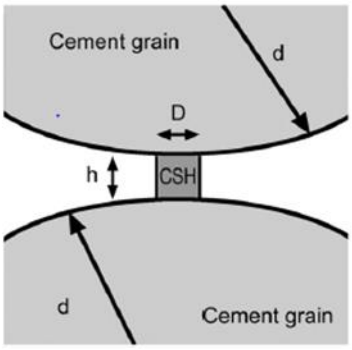

Figure 2-12:C-S-H bridge between two cement particles (Adapted from Roussel *et al*., 2012)

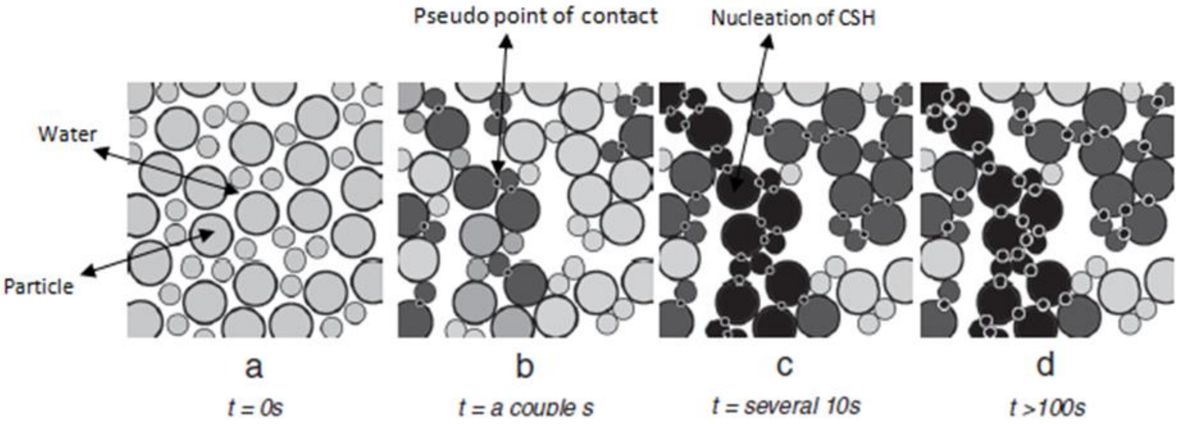

Figure 2-13: Development of cement paste rigidity: (a) cement particle dispersed in water, (b) nucleation of CSH and formation of interacting particle system, (c) formation of rigid network in the material (d) the size and number of CSH bridge increase and elastic modulus increases(Adapted from Roussel *et al.,* 2012)

2.4 Hydration kinetics modelling

The hydration reaction is a complex reaction that occurs with different stages and involves many influencing parameters. The mechanism of the hydration reaction is not fully understood in the open literature; however, there have been attempts to develop models that describe the hydration process more accurately and which give satisfactory results when compared to the experimental data. The following section will discuss the available hydration kinetics models as described in the literature.

2.4.1 Hydration kinetics

According to Arrhenius equation, the chemical affinity Aα can be expressed as:

$$A_\alpha = \frac{\alpha}{\eta_\alpha} exp\left(\frac{E_\alpha}{RT}\right), \qquad 2.12$$

where η_α, the permeability of the hydration products; *E*a: the activation energy (J); *R*: the real gas constant (J/mole K); and *T:* the temperature (Lin, 2006). From Equation 2.12, the rate of hydration can be written as:

$$\alpha = A_\alpha \eta_\alpha exp\left(\frac{E_\alpha}{RT}\right) \tag{2.13}$$

The affinity can be determined by the following equation:

$$A_\alpha = k\left(\frac{A_0}{k\alpha_u} + \alpha\right)(\alpha_u - \alpha) \tag{2.14}$$

The permeabilityη_α, can be written as:

$$\eta_\alpha = exp\left(-n\frac{\alpha}{\alpha_u}\right) \tag{2.15}$$

Therefore the hydration rate can be given by:

$$\alpha_\alpha = k\left(\frac{A_0}{k\alpha_u} + \alpha\right)(\alpha_u - \alpha)\times exp\left(-n\frac{\alpha}{\alpha_u}\right)\times exp\left(-\frac{E_\alpha}{RT}\right), \tag{2.16}$$

where *k, A_0* (initial affinity) and *n* are model parameters. This relationship provides the basis for further modelling of hydration kinetics.Based on the model developed by Lin (2006), the permeability was found to be mainly a function of the overall hydration; therefore, it can be expressed as:

$$\eta_\alpha = exp(-n\alpha) \tag{2.17}$$

The initial affinity A_0 can be correlated to the fineness of the cement, which is expressed in Blaine value (m^2/Kg) (Lin, 2006). A_0can be expressed by the following equation:

$$A_0 = \frac{A'_0\times Blaine}{350}, \tag{2.18}$$

where *A’₀*is the normalised initial chemical affinity of material hydration. It depends only on the chemical composition of the cement. The fineness of the cement affects the ultimate degree of hydration and the permeability of the cement. Lin (2006) found that the finer the cement, the larger the Blaine value and the smaller the size of the hydration products; therefore, the higher the permeability and the lower the parameter *n*. From this, the following relationship is obtained:

$$\eta_\alpha exp(1-\alpha)^2\, ln\left(\frac{350}{Blaine}\right) \tag{2.19}$$

Equation 2.19 shows that the effect of the Blaine number is not constant. At higher hydration rates, the effect of the Blaine number decreases (Lin, 2006).During the latter hydration period, the rate of cement hydration decreases at high temperature, so the parameter *n* should be a function of temperature *T*. Therefore using the volume ratio proposed in Equation 2.6, the effect of temperature on the parameter *n* can be shown as:

$$n\ \alpha\ \left(\frac{v_{293}}{v(T)}\right)^{10\ \alpha^4} \tag{2.20}$$

According to Lin (2006), the effect of hydrostatic pressure *p* is presumed to effect the chemical affinity $A\alpha$ only. The chemical affinity $A\alpha$ is represented by the correlation:

$$A_\alpha \alpha\ exp\left\{0.02\left(\frac{P}{P_{atm}}-1\right)^{0.07}\left[\frac{\alpha}{\alpha_u}-1.5\left(\frac{\alpha}{\alpha_u}\right)^2+0.4\right]\right\} \tag{2.21}$$

where the atmospheric pressure is p_{atm}. It has been shown that the reaction depends on the applied pressure *p*. Therefore the chemical affinity can be considered to be a function of the degree of hydration, the water/cement ratio, the Blaine fineness and the applied pressure *p*.

2.4.1 Ultimate degree of hydration for Portland cement

Research by Lin (2006) determined that the water/cement ratio and the fineness of the cement had an effect on the ultimate degree of hydration and that the ultimate degree of hydration α_u cannot exceed a theoretical value given by the following equation:

$$\alpha_u \le \frac{{}^{w}\!/_{c}}{0.4}, \tag{2.22}$$

where 0.4 is assumed to be the theoretical water/cement ratio needs for a full hydration. The ultimate degree of hydration is correlated to the curing temperature by:

$$\alpha_\alpha = \alpha_{u,293} exp[-0.00003(T-293)^2\ SGN(T-293)], \qquad 2.23$$

and

$$SGN(T-293) = \begin{Bmatrix} -1, When\ T \geq 293K \\ 1, When\ T < 293K \end{Bmatrix}, \qquad 2.24$$

and therefore the rate of hydration normalised can be written as:

$$\alpha = A_\alpha \eta_\alpha exp\left(\frac{E_\alpha}{RT}\right) exp\left(\frac{E_\alpha}{293R}\right), \qquad 2.25$$

where E_a is the apparent activation energy. A_α the chemical affinity, is expressed as:

$$A_\alpha\left(\alpha, \frac{w}{c}, Blain, P\right) = k\left(\frac{A_\circ}{k\alpha_u} + \alpha\right)(\alpha_u + \alpha)S(\alpha, p) \qquad 2.26$$

The function *S(α, p),* relates to the applied hydrostatic pressure *p*. The specific heat capacity of the cement paste q_{paste} is given by (Lin, 2006):

$$q_{paste} = \frac{M_{ce}}{\rho_{paste}}\left[\alpha q_{hce} + (1-\alpha)q_{ace} + \frac{w}{c} q_w\right], \qquad 2.27$$

where M_{ce}, amount (by mass) of cement in the paste (kg/m^3); q_{hce}: fictitious specific heat of the hydrated part of cement (J/(kg K)); q_{ace}: specific heat of the anhydrous cement (J/(kg K)); q_w: specific heat of water (J/(kg K)); and ρ_{paste}: density of cement paste (kg).Based on a thorough literature survey, no quantitative models have been obtained that describe the evolution of elastic modulus vs. time for blended cement paste. However, it is of interest to investigate whether or not the rheokinetic models used to predict the polymer curing process could be applied to characterise the hydration of blended cement.

2.5 Rheokinetics models to describe reaction of polymer curing

Hydration reaction, like all chemical reactions, can be defined using a specific kinetic reaction model. Various models are used to fit experimental data of hydration reaction until the best fit is found.For this research, three different kinetic models were considered and used to fit experimental data related to hydration reaction: the first order, the second order and the self-acceleration kinetics models.The first and second order kinetic equation can be defined in the following general equation:

$$dp/dt = K(1-p)^n, \tag{2.28}$$

where *n* is the reaction order; *K* is the reaction constant; *p* represents the extent of the reaction; and *dp* is the rate of the hydration reaction.

2.5.1 Reaction of first order

In the case of first order reaction, the following equation applies:

$$dp/dt = K(1-p) \tag{2.29}$$

In order to linearise this equation, the following integration is carried out:

$$\int (dp/(1-p)) = \int Kdt, \tag{2.30}$$

$$ln(1-p) = -Kt + c \tag{2.31}$$

In this case, the plot *-Ln (1 - p)* vs. *t* is used to fit experimental data and thereby determine whether the first order kinetic model is appropriate. A straight line plot will show that the kinetic model fits the data (Li *et al.,* 2000).

2.5.2 Reaction of second order

In the case of the second order reaction, Equation 2.28 above can be written as follows:

$$dp/dt = K(1-p)^2, \tag{2.32}$$

$$\int (dp/(1-p)^2) = \int Kdt, \tag{2.33}$$

$$1/(1-p) = Kt + c \qquad 2.34$$

To fit experimental data to this model, the plot 1/ (1-*p*) vs. *t* is used. As in the case of the first order reaction kinetics, a straight line would indicate a good fit of the experimental data by the model (Li *et al.,* 2000).

2.5.3 Self-acceleration kinetic reaction

In some cases, reactions cannot be defined based on the phenomenological equations of the n^{th} order for any sensible value of *n*. In such cases, reactions can be better defined by incorporating the self-acceleration factor:

$$d\beta/dt = K(1-\beta)(1-c\beta), \qquad 2.35$$

where β is the rheological degree of conversion; *t* is the time; *K* is the constant of the initial reaction rate at $\beta \rightarrow 0$; and *c* is the constant characterising the self-acceleration effect.

For reaction, different variants of self-acceleration reaction can be found. In the case of isothermal reactions, the following equation can be used:

$$d\beta/dt = Kf(\beta), \qquad 2.36$$

where $f(\beta)$ is the kinetic function that depends on the mechanism of the process.Since the rate of formation of products depends on the degree of conversion, the general rate of reaction, if taking place in different phases, can be written as follows:

$$d\beta/dt = Kf(\beta) + Kf(\beta)c, \qquad 2.37$$

which can be written as:

$$d\beta/dt = Kf(\beta)(1+c\beta) \qquad 2.38$$

It is very clear by deriving the equation that the mechanism of self-acceleration is caused by the phase separation and the reaction acceleration resulting from the increase in concentration of different functional groups (Malkin & Kulichikhin, 1996).According to Malkin and Kulichikhin (1996), another reason for initiating self-acceleration, might be due to the change in temperature. In fact, a local deviation from the isothermal nature of the process in a separated phase can occur. However, this cannot be considered as a significant violation of the isothermal conditions for the whole reactive mass since an important amount of solution surrounds the microgel.The integral of the equation for the first order reaction (i.e. if $f(\beta)$ = (1 - β)) can be written as follows:

$$ln\frac{(1+c\beta)}{(1-\beta)} = (1+c)Kt \qquad 2.39$$

For the second order (i.e. if $f(\beta)$ = (1 - β)^2) the integral of the equation is:

$$\frac{\beta}{1-\beta} + \frac{c}{1+c}ln\frac{(1+c\beta)}{(1-\beta)} = (1+c)Kt \qquad 2.40$$

During the process, there is a limitation movement of the elements causing deficient reaction, a phenomenon called the *effect of self-deceleration*. The development of these processes can be described by Equation 2.41:

$$d\beta/dt = K(1-\beta)(1-\varepsilon\beta), \qquad 2.41$$

where ε is the dimensionless parameter qualitatively reflecting the contribution of self-deceleration to the kinetics of the process.While self-acceleration is caused by an increase in reactant concentration in the separation phase, the self-deceleration is due to the acceleration of mobility in a system causing diffusional limitations for continuation of the reaction.

2.6 Summary

This research primarily investigates the hydration reaction of self-compacting concrete paste. The stages of hydration and the chemical reactions involved in each phase, as well as the effect of limestone and superplasticisers on hydration, have been discussed. However, in this review, the main focus was on limestone as this was the mineral additive used. The only chemical admixture used was the superplasticiser. Previous researchers obtained contradictory effects of limestone on cement hydration while superplasticisers have been unanimously observed to decrease the rate of hydration.The principal concepts of cement paste rheological properties were introduced, followed by a detailed discussion of the basic theory underlying the rheological properties of cement paste. Different measurement methods have also been identified and discussed. Various rheological parameters related to the cement paste, such as storage modulus, loss modulus, loss factor and complex modulus, including their implications on the workability and the flowability of the cement paste, were discussed in this section.

This review also presents the kinetic model describing the hydration based on previous work. Various factors affecting the hydration kinetics of SCC, including the chemical composition of the cement paste, the curing temperature as well as the reaction affinity of the cement and water, were considered in developing the model. However, some observed phenomena during hydration cannot be adequately explained using this model, especially in the case of SCC with various mineral and chemical admixtures. Therefore, it needs to be modified or optimised to fit the observed results from the hydration reaction of Portland SCC. Besides, no quantitative measure has been applied to correlate the hydration kinetics to the evolution of elastic modulus in the study of the rheological properties of cement paste. This, then, constitutes one of the major objectives of this research.

There is a dearth of information concerning the influence of different admixtures on the hydration kinetics of cement paste in literature, and the available models to describe the hydration kinetics are not practical and simple to interpret. Consequently, it is necessary to investigate the effect of the mineral admixture on the kinetics of cement paste hydration using a simple kinetic model.

Chapter 3. Experimental work

3.1 Introduction

This chapter provides a comprehensive description of the experimental procedure used in this work. The experimental work was conducted with the purpose of determining the effect of cement properties, superplasticiser concentrations and limestone dosage on the rheological parameters (elastic modulus) which influence the performance of self-compacting concrete paste (SCCP) in terms of hydration.The type of materials used – such as cement, limestone and superplasticiser – will be discussed, as well as the various preparation methods followed. The binary and ternary mixtures were each compared to the baseline mix composed of pure cement paste only. The components for each mix were obtained by using these materials in different proportions to produce a self-compacting cement paste. Since cement paste is a time-dependent material, and so its rheological properties change over time, the growth of the elastic modulus over time was monitored to investigate the microstructural change occurring during hydration.

The measurement of elastic modulus was done in dynamic mode using a rotational rheometer with roughened parallel plate geometry.The self-acceleration kinetic equation was used to describe the hydration reaction of self-compacting concrete paste (SCCP). From the results obtained, other parameters were determined such as characteristic time, self-acceleration kinetics and real time. The work was conducted at the CPUT Flow Process and Rheology Centre (FPRC).

3.2 Materials and matrix of samples

3.2.1 Cement

The four cements used for the experimental work were CEM1 52.5 N, obtained from one manufacturer but produced at different factories in South Africa. These cements had different physical, chemical composition and mineralogy but all were Ordinary Portland Cement (OPC).The four cements, named C1, C2, C3, and C4, had different chemical properties, as shown in Table 3.1. Na_2Oeq is the alkali equivalent of the cement determined according to an equation proposed by Mohammed and Asmaa (2010). According to Rietveld, analysis of XRD the mineralogy compounds are shown in Table 3.2. The physical properties are presented in Table 3.3.

Table 3-1: Chemical properties of the four cement types

Chemical Oxides	**C1**	**C2**	**C3**	**C4**
SiO_2	20.8	21.4	21.1	22.4
Al_2O_3	3.8	4.2	4.0	4.8
Fe_2O_3	2.9	2.8	3.0	3.3
Mn_2O_3	0.1	0.7	0.6	0.4
TiO_2	0.2	0.3	0.3	0.5
CaO	64.0	62.9	62.9	61.6
MgO	1.2	3.3	2.9	2.6
P_2O_5	0.17	0.10	0.03	0.11
SO_3	2.33	2.61	2.74	2.88
Cl	0.00	0.00	0.00	0.00
K_2O	0.66	0.36	0.24	0.24
Na_2O	0.34	0.19	0.15	0.18
Na_2Oeq	0.75	0.41	0.29	0.33
LOI	4.11	1.84	2.83	1.77
Total	100.5	100.7	100.8	100.7
FCaO	1.00	1.27	0.95	1.41

Table 3-2::Mineralogy compounds of the four cement types (XRD)

Minerals present (%)	**C1**	**C2**	**C3**	**C4**	**Chemical Formula**
Calcium Silicate (C_3S)	59.92	50.80	52.74	54.19	Ca_3SiO_5
Larnite (C_2S)	13.99	20.43	18.76	17.95	$Ca_2(SiO_4)$
Calcium Aluminium Oxide (C_3A)	3.95	2.75	1.84	2.63	$Ca_3Al_2O_6$
Brownmillerite (C_4AF)	14.54	18.46	20.49	17.15	$FeAlO_3(CaO)_2$
Periclase	1.00	2.92	2.08	2.49	MgO
Lime	0.35	0.41	0.51	0.40	CaO
Arcanite	1.37	0.78	0.31	1.34	K_2SO_4
Gypsum	1.62	2.74	2.92	1.29	$CaSO_4.2H_2O$
Bassanite	3.28	0.63	0.35	2.58	$CaSO_4.0.5H_2O$

Table 3-3Physical properties of the four cement types:

Physical properties		C1	C2	C3	C4
Relative density pyc	Relative density pyc	3.05	3.03	3.04	2.99
Specific Surface	Reported S/Surface,	3750	3650	4250	3850
Std Cons Cement	Std Consistence, %	25.0	31.0	25.0	33.0
Setting Time	Initial Set, min	170	180	190	315
	Final Set, h	3.25	3.75	3.75	6.00
32 μm Residue	32 μm, %	-	-	-	-
45 μm Residue	45 μm, %	11.7	0.6	3.9	1.8
90 μm Residue	90 μm, %	1.1	0.0	0.5	0.1
212 μm Residue	212 μm, %	0.2	0.0	0.0	0.0

3.2.2 Limestone

This component, also known as Kiln dust, Cyclone dust, Cycal or Dolomitic kiln dust, is mainly composed of limestone or calcium carbonate, but contains other elements such as magnesium oxide, calcium magnesium carbonate and crystalline silica. Limestone is a viscosity modifying agent and can be used as filler. It can improve the workability of the concrete by increasing its flowability. The chemical properties of limestone are given in Table 3.4 and its physical properties in Table 3.5.

Table 3-4:Chemical properties of limestone

Chemical	Limestone
SiO_2 (%)	8.42
Al_2O_3 (%)	0.32
Fe_2O_3 (%)	0.57
Mn_2O_3 (%)	0.01
TiO_2(%)	0.05
CaO(%)	49.23
MgO(%)	0.65
P_2O_5(%)	0.16
Wet SO_3(%)	0.20
Wet Cl (%)	0.04
K_2O (%)	0.30
Na_2O (%)	0.28
LOI (%)	39.76
Total (%)	100
FCaO(%)	-
IR (%)	-
Cl (Ppm)	-
Reactive SiO_2(%)	-

Table 3-5:Physical properties of limestone

Physical properties		Limestone
Relative Density Pyc	Relative Density Pyc	2.62
Specific Surface	Reported S/Surface, cm^2/g	1850
32 μm Residue	32 μm, %	49.0
45 μm Residue	45 μm, %	28.9
90 μm Residue	90 μm, %	1.5

3.2.3 Superplasticiser

Superplasticiser, also called a water reducing agent, reduces the use of water in the paste. Superplasticisers are chemical admixtures that can be added to cement mixtures to improve their workability. Depending on the proportion of water reduction, these chemicals can be classified as plasticisers or superplasticisers.Two types of superplasticisers were obtained from different manufacturers for this project, namely SP1 and SP2 (Table 3.6). SP1 was a modified acrylic polymer and SP2 was polycarboxylate chemical based. In this study, two SPs were investigated whose molecular structure characteristics are shown Figure 3.1. Both SP1 and SP2 were characterised based on the correlation between the carboxyl group and absorption intensity to ascertain their molecular structures.

Table 3-6:The characteristics of the two types of superplasticiser

Characteristics	SP1	SP2
Consistency	Liquid	Liquid
Colour	Amber	Brown-green
Density according to ISO 758 (g/cm^3)	1.07 ± 0.02	1.05 ± 0.02
Dry content according to EN 480-8 (%)	26 ± 1.3	20.3 ± 1
Chlorides soluble in water according to EN 480-10 (%)	<0.1	≤ 0.1
Alkali content (Na_2O equivalent) according to EN 480-12 (%)	<2.5	≤ 1.0

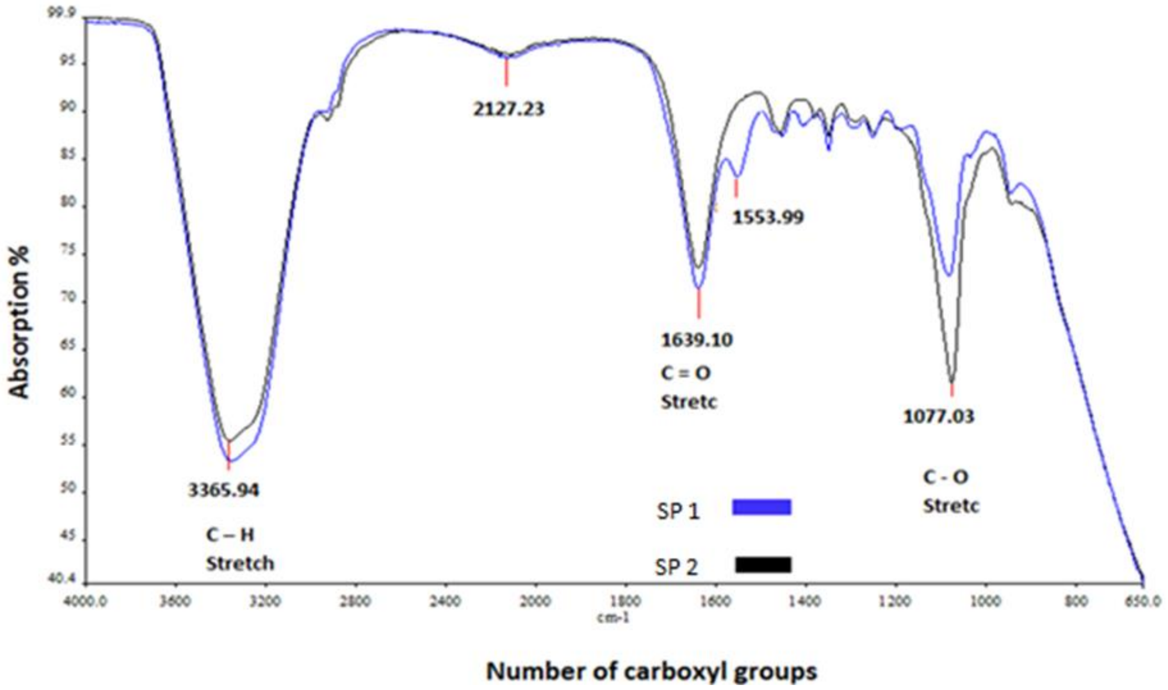

Figure 3-1:Infra rouge spectrum analysis for SP1 and SP2

3.3 Preparation of cement admixture

This section provides details concerning the preparation of samples before the rheological measurements. The mixing protocol regarding various combinations of these materials is also presented. Figure 3.2 illustrates the matrix set for this investigation.

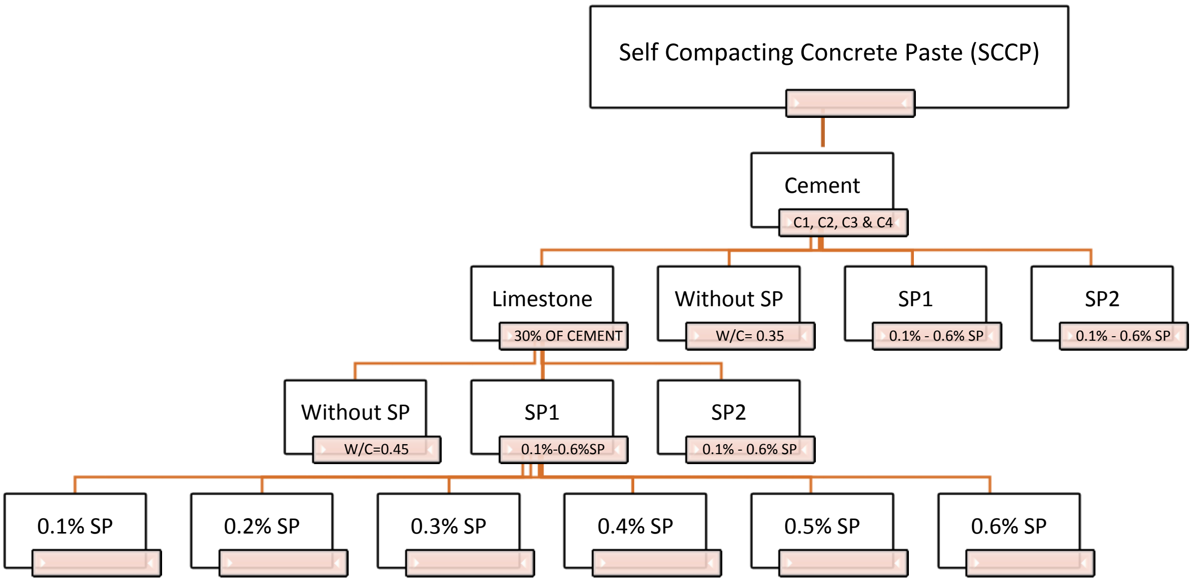

Figure 3-2:Matrix of cement paste samples

When conducting experiments with ‘living systems’, it is necessary to establish clear reference points to ensure the reproducibility of the measurements. Measures and guidelines are therefore needed when preparing experimental samples and when conducting the experiments. The experiments were all conducted at controlled room temperature and humidity. The cement paste and mixture was prepared by mixing cement, limestone, water and superplasticiser at different ratios.The cement was delivered from the supplier in 22 kg buckets. Four cements produced by one manufacture were provided (C1, C2, C3 and C4). The four cements were CEM1, but different in their physical properties, chemical composition and mineralogy, as shown in Table 3.1, 3.2 and 3.3.

Two types of superplasticisers, namely SP1 and SP2, acquired from different manufacturers were used in the sample preparation.In previous work the saturation of polycarboxylate based SP has been found to reach its saturation at 0.3% (Mbasha et al., 2015). The interest of this research was to found out what happens before and after this saturation point when using limestone. This is why the SP dosage was varied from 0-0.6% considering 0.3% the center point. In addition, after 0.6% the suspension becomes much diluted without exhibiting any features of SCCP.

For the purpose of tests, two types of samples were prepared, first with limestone and the second without limestone.Different dosages of limestone and water cement ratios were tested until the optimum quantities of both parameters were found. The range of limestone concentration used during these tests was obtained from previous works conducted by Mebrouki *et al*. (2009). The water/cement ratios used were also taken from literature to ensure that the appropriate ratio for self-compacting paste was used for the project (Yahia *et al.,* 2005).In case of admixture with the limestone, the following mixtures were prepared (Figure 3-3):

- 135 gm of cement was used.
- Limestone added at a value of 30% of cement corresponding to 40.5 gm.
- Water/cement ratio was chosen as 0.45.
- Superplasticiser concentration in the mix was varied from 0% to 0.6% of cement and limestone mixture by mass.

Figure 3-3:Sample preparation

Mixing was required to increase the homogeneity and preserve the cement paste structure while reducing the risk of forming agglomerations which would prevent water from reaching all the particles. Intensive mixing by hand was carried out in this research, in agreement with the work conducted in Nachbaur *et al.* (2001), Williams *et al.* (1999), Yang and Jennings (1995) and Asaga and Roy (1980). All samples were mixed manually for two minutes in order to maintain a level of consistency in the experiments.Limestone was dry mixed with the cement. The water/cement ratio for all the tests of admixture with limestone was kept as 0.45. As superplasticiser was added the amount of water was reduced accordingly. The water and superplasticiser were mixed and then added to the dry mix (cement and limestone) and stirred by hand for two minutes. This procedure was followed for each type of cement and superplasticiser as shown in Table 3.6.

In case of admixtures without limestone, the following mixtures were prepared:

- 135 gm of cement was used.
- The water cement ratio was set at 0.35 corresponding 47.25 gm.
- The superplasticiser was varied from 0% to 0.6% of the cement.

The water/cement ratio for all the tests of admixture without the limestone was kept as 0.35. The water and superplasticiser, once mixed, were gently added to the cement over two minutes of mixing. This method of preparation was carried out for all cements and superplasticisers and mix proportions for paste with and without limestone are presented in Tables 3.7 and 3.8.

Table 3-7::Admixtures for cement paste with limestone

Cement (g)	**Limestone (g)**	**Water (g)**	**Superplasticiser (g)**
135	40.5	60.75	0.00
135	40.5	60.57	0.18
135	40.5	60.40	0.35
135	40.5	60.22	0.53
135	40.5	60.05	0.70
135	40.5	59.87	0.88
135	40.5	59.70	1.05

Table 3-8:Admixtures for cement paste without limestone

Cement(g)	**Water(g)**	**Superplasticiser(g)**
135	47.25	0
135	47.11	0.14
135	46.98	0.27
135	46.85	0.40
135	46.71	0.54
135	46.57	0.68
135	46.44	0.81

3.4 Measuring equipment

A Paar Physica (MCR-51) rotational rheometer was used for the experimental work with an operating temperature maintained at 25℃ (Figure 3.4). According to Fernàndez and Casanova (2006), the rheological properties of the cement paste are not influenced by the temperature in the range between 5 and 25℃. Petit et al. (2009) reported changes in rheological properties within this temperature range. For this investigation all the work was done at controlled temperature. This rotationanl rheometer is suitable for rotational or oscillatory mode. According to Nehdi *et al*. (2004), the difficulties in studying the rheological properties of a living system such as cement paste are to select the proper equipment for the experiment, the compatible gap and friction level of the surface, to follow the sampling protocol systematically and to define an appropriate technique for rheological measurement.

Figure 3-4: Paar Physica MCR-51 Rheometer

3.5 Experimental apparatus

For the purpose of this project, a rough surface plate was used rather than smooth for storage modulus measurement due to the risk of slippage of cement paste during the experiment (Banfill, 2003). An electronic scale was used to weigh all the material, including cement, limestone, superplasticiser and water. A stop watch was used to observe the preparation time of the sample.The gap between the parallel plates was set to 0.7 mm based on previous experiments at a value twice the measured particle size value (Ferraris & Gaidis, 1992). While various measuring gaps had been used in previous work, the gap used in this project was considered as within a reasonable range compared to those cited in literature and as used in the experiments of Nehdi and Rahman (2004).In order to determine the range for the storage modulus test, frequency sweep and amplitude sweep tests were carried out based on tests conducted in previous work by Papo and Piani (2004) and the values obtained were in agreement with those found in literature.

The amplitude sweep was done with an amplitude range from 0.1 to 1.5%, while keeping the frequency constant at a value of 0.1 Hz, as used by Papo and Piani (2004).The frequency sweep was done with amplitude set at 0.2%, while the frequency was varied from 0.1 to 1 Hz and the value of 1 Hz was selected.The strain applied on the test was kept below the yield stress value to maintain the integrity of the material structure.

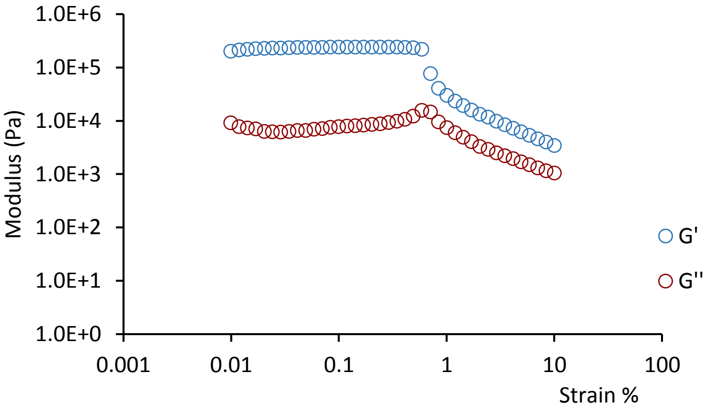

Figure 3-5: Small amplitude oscillation measurements

Data from Figure 3.5 make clear that a break in the microstructure formed at 0.6% strain, which is large amplitude, affecting the agglomeration evaluation using oscillatory methods, and so influencing the evaluation. Therefore 0.2% strain was chosen for this experiment to maintain the integrity of the material structure.This approach of using small amplitude oscillation measurements is supported by Lootens *et al*. (2004) who stated that the coagulated network (product of the gelation of the cement paste) has a poor mechanical strength and can be destroyed by mixing although it is strong enough to have a measurable yield stress. This emphasised the need to use small amplitude during experimental work, as was also the case in the work conducted by Bellotto (2013) where small amplitude oscillation measurements were preferred for experimental work.

3.6 Experimental procedure

The storage (elastic) modulus evolution in time *G'(t)* was chosen as the main experimental focus for following the hydration kinetics, at room temperature and ambient humidity. All measurements were carried out in the linear viscoelasticity domain (at low shear deformations). The independence of the storage modulus on the amplitude deformation (i.e. linearity of behaviour) was specially investigated.

The storage modulus was measured using the parallel plate technique. Proper procedure was followed to ensure all the samples were measured under the same conditions with respect to sample compositions, device parameters and measuring time. The parallel plate technique was used as follows:

3.6.1 Time sweep (elastic modulus)

The elastic modulus measurements were carried out with the Physica MCR51 (Anton Paar) rotational rheometer with a sand blasted plate-plate operating unit with plate diameter of 50 mm at 25º C. Experiments were performed at the frequency of 1 Hz and the amplitude was fixed at 0.2%. The gap size was 0.7 mm. The selected plate was inserted on the rheometer and the device set up properly. Samples were prepared by mixing cement, water, superplasticiser and limestone manually for duration of two minutes. Then the mixed sample was placed on the lower plate, the gap between plates was 0.7 mm. A pre-shear of 50/s for 60 s was executed in rotational mode prior to the storage modulus measurements. Measurements were taken until storage modulus value became constant (or reached equilibrium).The upper plate was then lifted to a height of 70 mm and both plates were cleaned. Then the identical procedure was followed for the next sample.

3.7 Measured variable

The performance of self-compacting concrete (SCC) is highly dependent on the rheological properties of self-compacting concrete paste (SCCP) systems. Cement pastes are characterised by constantly changing structures which change their rheological properties. As the hydration proceeds, the cement paste continuously evolves from fluid to solid. The cement paste rheological properties are therefore dependent on hydration reaction while the rate of hydration is directly influenced by the clinker, the main component found in cement. The hydration of cement of varying composition is complex and affects concrete production. This can be studied through the hydration kinetics of SCCP with various admixtures.

According to Nachbaur *et al*. (2001), the dynamic mode rheology is the most effective way of investigating the internal microstructures and the inter-particle forces that are directly related to the cement paste properties. This method is particularly preferred as it is carried out in the linear viscoelasticity domain, thereby avoiding the breakdown of structures and allowing the hydration reaction to proceed unperturbed. Dynamic Oscillatory shear tests can be separated into two regimes. The first regime is a linear viscoelastic with small amplitude oscillatory shear (SAOS), and the second regime is nonlinear material with large amplitude oscillatory shear (LAOS). As the frequency is kept constant and the amplitude (strain and stress) increased, Figure 3-6 data makes clear that there is a break in the microstructure marked by the transition from linear to nonlinear regimes, at a large amplitude (critical strain). This affects the agglomeration evaluation using oscillatory methods (Hyun *et al*., 2011).

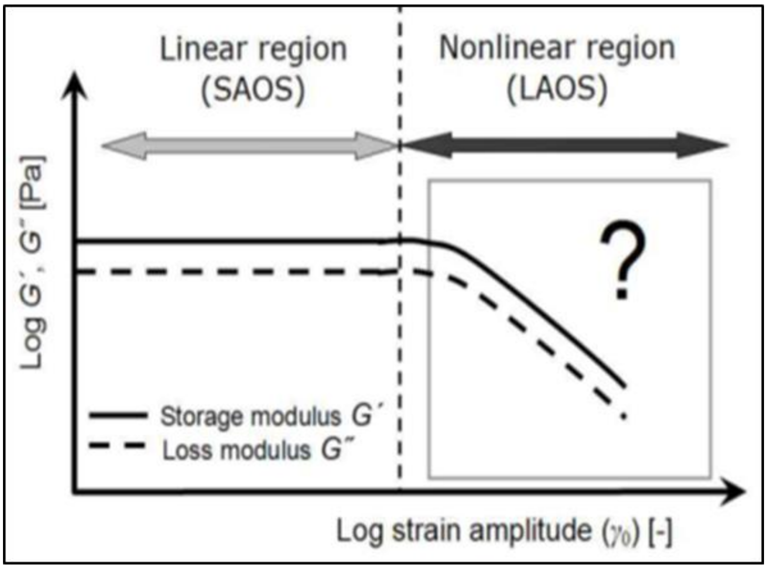

Figure 3-6:Dynamic Oscillatory shear test (Hyun *et al.,* 2001)

According to Banfill (2006), cement paste is a viscoelastic material and the rheological behaviour of all viscoelastic materials consists of two components: the viscous portion performed by the loss modulus and the elastic portion performed by the storage modulus. The loss modulus *G"* measures the deformation energy lost in the process which will not be recovered at the end. The storage modulus represented by *G'* measures the deformation energy contained in the material in the beginning of the shear process. As discussed in Chapter 2, these two portions represent vectors located in the x and y axes respectively. The length of each represents the value corresponding to that parameter. The sum represents a new parameter called the complex modulus represented by *G**. The complex modulus is therefore the resultant vector of both *G'* and *G"* vectors as illustrated in chapter 2 (Figure 2.4). *G** therefore reflects the complete viscoelastic behaviour of a material.

For an ideal solid material, the loss modulus *G"* is considered to be zero. This means that there is no loss in energy since the material is totally elastic. In this case δ = 0°, the complex modulus *G** is defined as *G'*. However, for an ideal liquid material, *G'* is equal to zero since there is no rigidity present in liquids. Consequently, δ =90°, *G** is defined as *G"* (Schultz

&Struble, 1993). For δ= 45°, there is a perfect balance between the viscous *G"* and the elastic *G'* forces (Mezger, 2002). Figures 3.7 and 3.8 illustrate clearly the different phase angles according to the properties of the material.

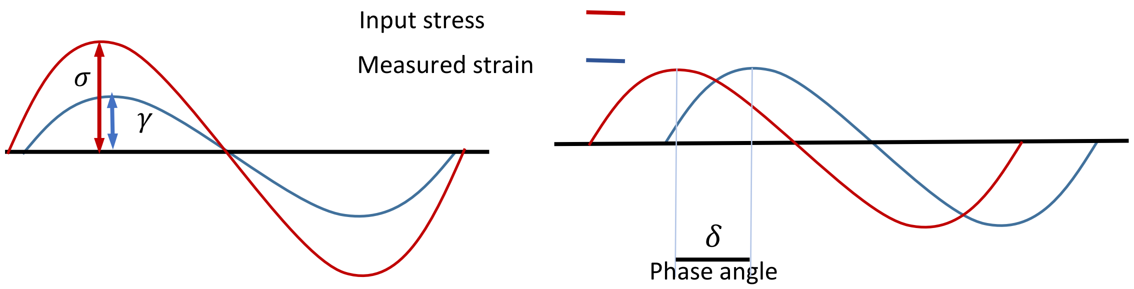

Figure 3-7: Phase angle (δ)

Elastic material: solid-like behaviour

- The stress and strain are exactly in phase.
- Therefore, the phase angle is zero.

Viscous material: liquid-like behaviour

- The stress and strain are ¼ of a cycle out of phase.
- Therefore, the phase angle is 90°.
-

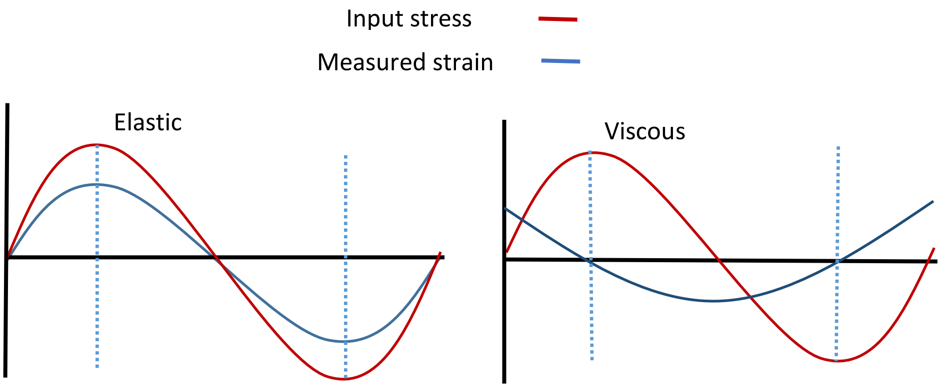

Figure 3-8: Phase angle for elastic and viscous material

The cement paste exhibits more elastic than viscous behavior; the complex modulus is therefore characterised by the storage modulus. Thus the measured variable can be referred to as the storage modulus. Based on previous work by Bellotto (2013), the elastic modulus displays different behaviours as the hydration proceeds. During the hydration process, a paste can be considered as a colloidal medium with increasing attractive interaction of dispersed particles and these forces are responsible for the elasticity of a material. It has been found that elastic modulus shows a rapid increase from 10^1 to 10^5 Pa (Kirby & Lewis, 2004), an increase due to changes occurring within the flocculated networks between cement paste particles. In order to determine the evolution of the cement paste hydration, it is necessary to observe the evolution of the elastic modulus of the cement paste over a long period of time.

3.8 Summary

The equipment for a proper collection of elastic modulus results was readily available in the rheological laboratory of the Flow Process and Research Centre. A MCR-51 rheometer was used for the purpose of these experiments. The apparatus was described and its operating mode detailed in this section. The settings selected made it possible to record the desired rheological parameters of the cement paste admixtures tested with optimum accuracy. Various types of rheometers were available with different geometry, such as the coaxial cylinder and the parallel plate types. The coaxial cylinder type was not selected due to the risk of cement paste settlement during testing. This risk was significantly lower for the case of the roughened parallel plate rheometer.

The parallel plate technique was used for all the elastic modulus measurement. The value of the strain was set at 0.2% resulting in stress below the yield stress and the angular frequency was set at a constant value of 1 Hz. The gap between the two plates was set at a value of two times the particle size. The rough surface type of parallel plate was used instead of the smooth one for all measurements. The temperature was maintained at 25 ℃ for all measurements.Samples made of cement, limestone, superplasticiser and water at various amounts and ratios were used during the experiments. The two types of samples used in this work were the cement paste admixture with and without limestone. The water/cement ratio was varied depending on whether or not limestone was added.

Chapter 4. Results and discussion

4.1 Introduction

The subject of this study was the evolution of the rheological properties of cement pastes up to moment of setting, as discussed in Chapters 2 and 3. The rheometry in dynamic mode was used to investigate the properties of the cement paste in the dormant phase of hydration. Time sweep techniques were used to evaluate the elastic behaviour of the cement pastes.In order to analyse the rigidification process of cement paste, it is necessary to observe the evolution of the elastic modulus of the cement paste over time. This chapter presents information on the changes that occur in the cement paste microstructure during hydration.

4.2 Time sweep

During hydration, the microstructural changes that take place within the paste are due to the increase in magnitude of attractive forces between cement particles, forces which govern the rheological properties of cement paste during the early age of hydration and dictate the rigidification of the cement paste (Bellotto, 2013). Cement pastes have constantly changing structures; hence, their rheological properties evolve over time. As the hydration proceeds their structure changes from fluid to solid. This setting process has been thoroughly researched and is attributed to the products of hydration such as C-S-H. It is therefore clear that rheological properties of cement paste depend primarily on the hydration of cement (Hildago *et al.,* 2008).

Nachbaur *et al.* (2001) suggested that the effect of hydration on the rheology of cement paste be investigated in the dynamic mode. When carried out within the linear viscoelastic domain this is a non-destructive approach as it does not destroy the link between particles nor disturb the kinetics of hydration. This research focused solely on the rigidification of cement paste in the dormant phase of hydration. The solidification of cement paste is characterised by the formation and the precipitation of C-S-H causing a sharp decrease in the rate of hydration and an increase in the magnitude of interactive forces between particles (Bellotto, 2013).Earlier investigations have found that elastic modulus displays different behaviours as hydration proceeds. In the dormant period, the elastic modulus displayed higher growth over time if the paste is not sheared (Bellotto, 2013). It was considered that this increase was due to changes occurring within the flocculated networks between cement paste particles.

Many researchers have used some chemical admixtures and supplementary cementitious materials – such as superplasticisers, limestone, fly ash and slag – to improve the rheological properties of cement pastes for a better performance of self-compacting concrete (Sahmaran *et al*., 2006).

This section presents the results of the investigated cements (C1-C4) in the presence and absence of limestone (LS) at different concentrations of two different superplasticisers (SP1 and SP2).

Effect of SP1 on cement pastes without limestone

The elastic modulus was observed over a period of time. The effect of SP1 on the rheological properties of cement paste was assessed by considering the evolution of the elastic modulus at different concentrations (i.e. from 0% to 0.6%) of SP1. Figure 4.1 illustrates the kinetics of the elastic moduli of all cements with SP1. The same time-scale was used for each case to determine the differences in the hydration process between various cement samples. It can be seen from Figure 4.1 that the elastic modulus displayed three different stages as the hydration proceeds: retardation, fast acceleration and the final plateau.

The effect of SP is evident on these graphs. Firstly, the initial values of *G’* are decreased with the introduction of SP1 within the paste. Also, the retardation zone increased with the increase in concentration of SP1. As time of hydration increased, the samples reached a plateau, but with different values of *G’* depending on the cement and concentration of SP. The time required to reach the plateau varied with each concentration of SP1. This plateau could indicate a certain internal equilibrium reached within the paste; thus causing no more variations in *G’* values.

In the absence of SP, the initial values of *G’* for all cements were higher compared to the case of cements with SPs. These initial values were proportional to the increase of the SP concentration and were in agreement with the findings of Kirby and Lewis (2004). The initial values of *G’* for all cements are presented in Table 4.1.

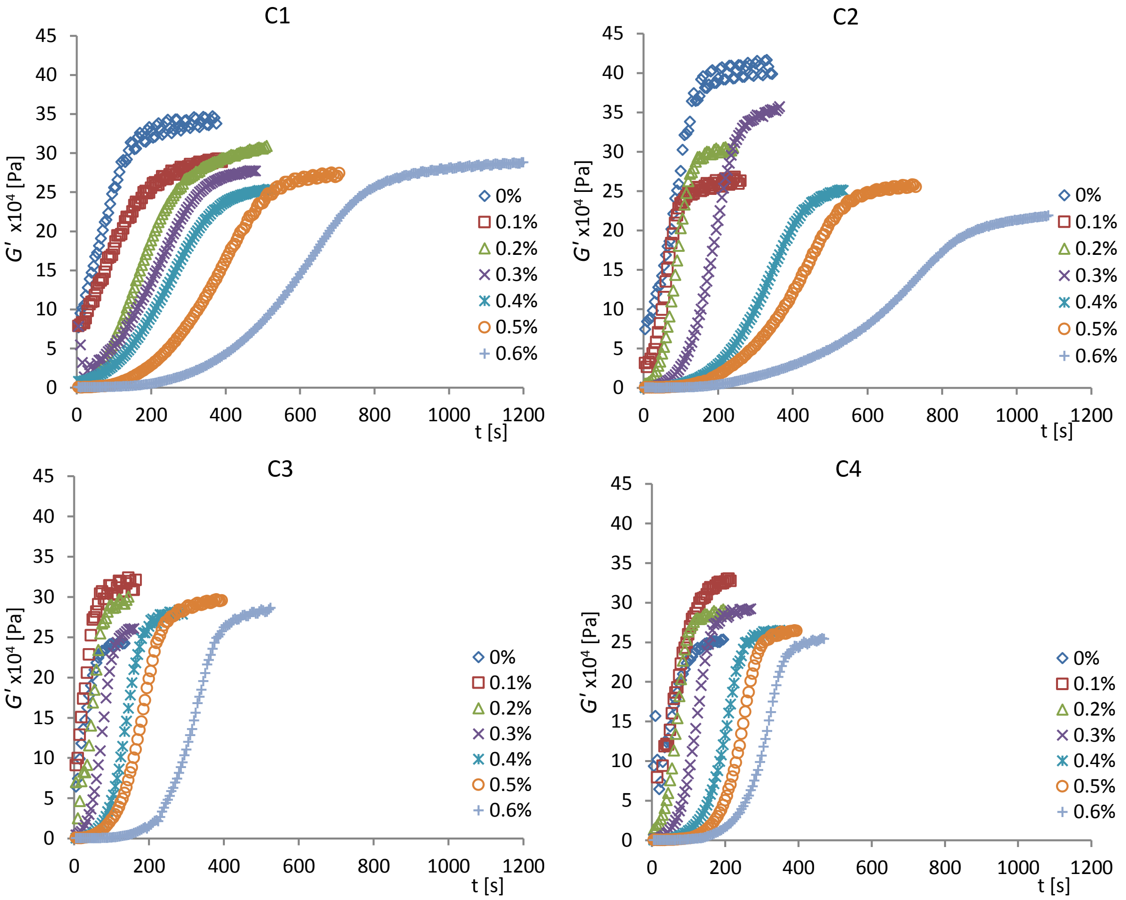

Figure 4-1: Elastic modulus evolution for the four cements with different concentrations of SP1 (0% - 0.6%)

Table 4-1: Initial value of *G'* for each cement at different concentrations of SP1

Initial value of *G'* x10^4 (Pa)				
Concentration of SP1, %	**C1**	**C2**	**C3**	**C4**
0	16.8	10.9	14.7	10.2
0.1	8.9	4.9	18.6	7.9
0.2	0.9	1.6	8.2	3.2
0.3	0.7	0.2	1.7	0.5
0.4	0.9	0.05	0.2	0.1
0.5	0.1	0.04	0.14	0.03
0.6	0.06	0.03	0.03	0.02

As far as the time of hydration of the pure cement paste is concerned, C1 and C2 had the longest period of increasing *G'* value before reaching their plateau, followed by C4, and the shortest time of increase in *G’* values was observed for C3. The addition of superplasticiser contributed to the decrease in the initial value of *G’* and an increase in the hydration time required to reach the plateau. With an increasing SP1 dosage for each cement, the time to reach the plateau also increased.At the same concentration of SP1, cements C1 and C2 had the longest hydration time while cements C4 and C3 exhibited the shortest time. In the absence of SP, the highest *G’* value before reaching a plateau was experienced by C2 and was estimated at 42 x10^4 Pa, followed by C1 with 34.7 x10^4 Pa, and C4 with 25 x10^4 Pa, while the lowest value was observed in the case of C3 being estimated at 24 x10^4 Pa.With the addition of SP1 at the highest concentration (0.6%), the highest *G’* value before reaching a plateau was experienced by C1 and was estimated at 30 x10^4 Pa, followed by C3 at 28.7 x10^4 Pa, and C4 at 25.4 x10^4 Pa, while the lowest value was observed in the case of C2 and was estimated at 22 x10^4 Pa.

Effect of SP2 on cement pastes without limestone

As in the case of SP1 dosages, the effect of different dosages of SP2 from 0% to 0.6% on the four cements is given in Figure 4.2. Figure 4.2 shows an increase in the duration of the initial and dormant period with increasing superplasticiser dosages. However, this increase was not uniform for the different concentrations of SP2 for each cement. Figure 4.2 reveals that the addition of SP2 at low concentrations had little effect on the times of hydration required to reach the plateau. However, at higher SP2 concentrations the time to reach the plateau increased accordingly. The addition of SP2 within the paste decreased the initial value of *G’* as well (Table 4.2). The highest values of elastic modulus were observed at 0% of SP2 for the four cements.

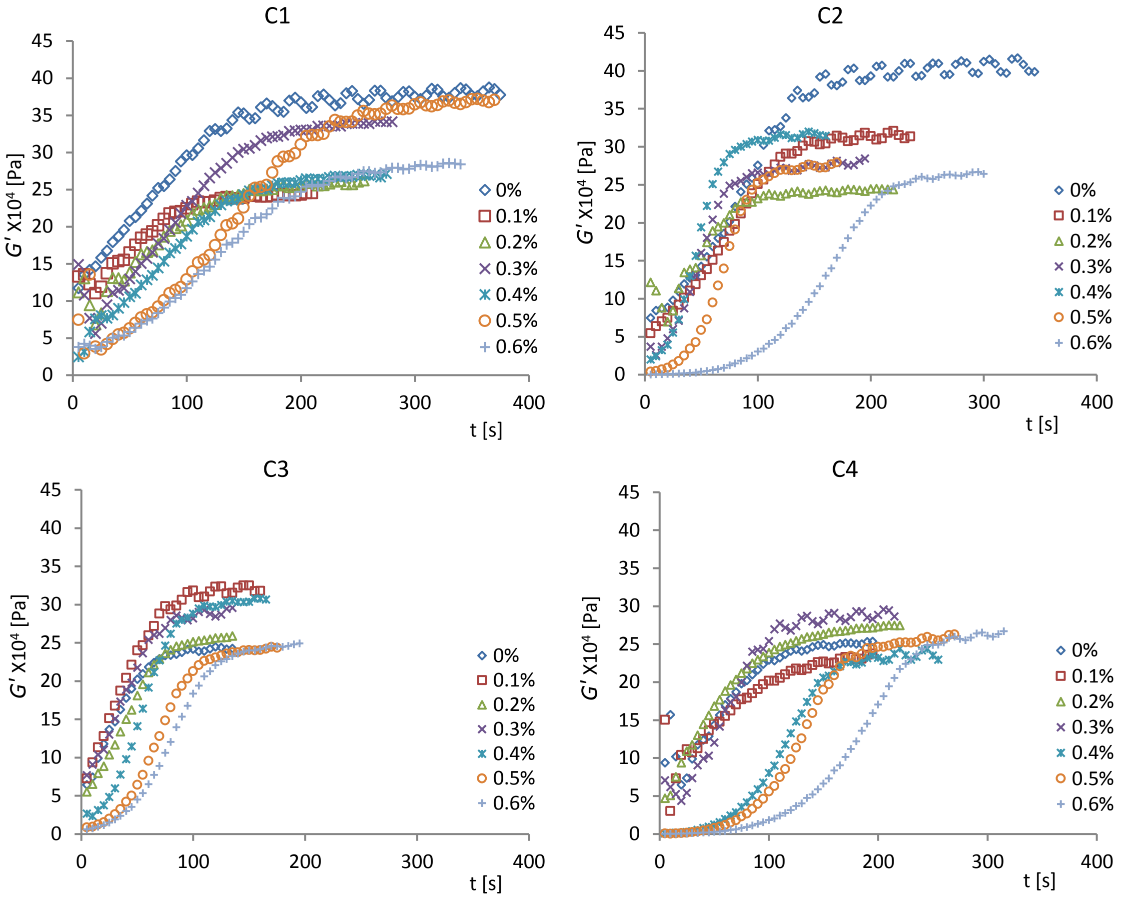

Figure 4-2: Elastic modulus evolution for the four cements with different concentrations of SP2 (0% - 0.6%)

Table 4-2: Initial value of *G'* for each cement at different concentrations of SP2

Initial value of *G'* x10^4 (Pa)				
Concentration of SP2, %	**C1**	**C2**	**C3**	**C4**
0	16.8	10.9	14.7	10.2
0.1	13.7	7.5	12.8	7.3
0.2	11.3	7	11	7.5
0.3	9.5	4.8	8.9	5.3
0.4	7.7	3.9	3.8	0.2
0.5	4.2	0.9	1.5	0.06
0.6	4.5	0.1	1.2	0.04

The presence of SP2 within the cement paste affected cements differently as compared to SP1. In the presence of SP2, the hydration rate was the lowest for C1 and C4 and was followed by C2 and C3 respectively. With increasing SP2 dosages for each cement the time required to reach the plateau also increased especially for high concentrations.For the same concentration of SP2 for each cement, cements C1 and C4 had the longest hydration time before reaching a plateau, followed by cements C2 and C3 respectively. The addition of SP2 had slightly different effects on *G’*.In the case of the highest concentration of SP2 (0.6%), C1 exhibited the highest value of *G’* before reaching the plateau at 29 x10^4 Pa, followed by C2 at 26.7 x10^4 Pa, C4 at 26.7 x10^4 Pa, and C3 at 25 x10^4 Pa.In general, it can be seen that the effect of SP1 on cement hydration is more predominant than the effect induced by SP2. However, the difference in rheological behaviour of all cements in the presence of SPs could be due to their chemical and physical interaction during the hydration.

Effect of limestone on cement pastes

Limestone

Limestone is an important mineral filler, widely used in the construction industry. Therefore, it was important to investigate the impact of adding limestone on the hydration of self-compacting concrete paste. A mixture was prepared consisting of limestone and SP at different concentrations in the cement paste.

Cement paste with limestone with SP1

Figure 4.3 shows the effect of *G'* over time for different concentrations of SP1. The effect of different dosages of SP1 from 0% to 0.6% on the elastic modulus of each cement with the addition of limestone is given in Figure 4.3.

It can be seen that even with the addition of limestone, the time required to reach the plateau was increasing with an increasing SP1 dosage. The highest initial value of the elastic modulus for the four cements was 0% for SP1 and the lowest value was for cements with the highest concentration of SP1 (0.6%) (Table 4.3).

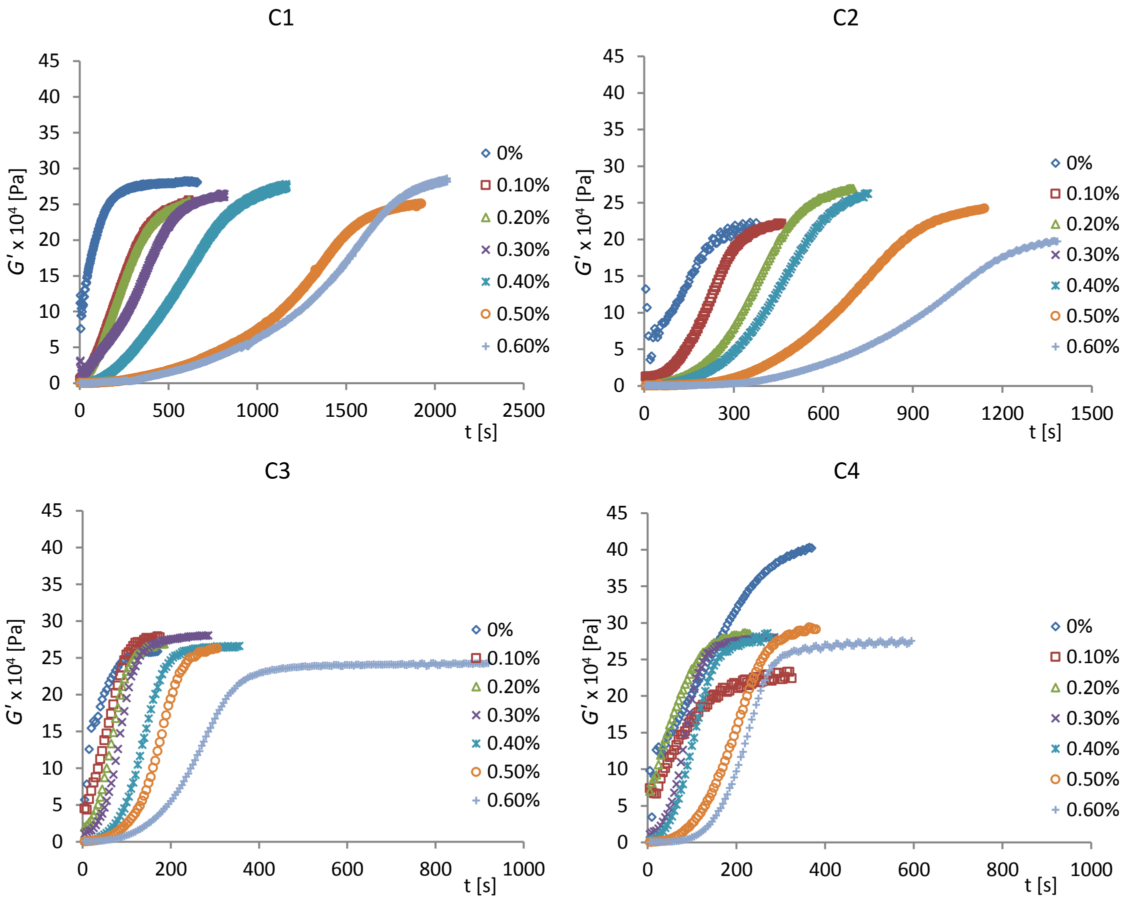

Figure 4-3: Elastic modulus evolution for the four cements with different concentrations of SP1 (0% - 0.6%) with addition of limestone

Table 4-3: initial value of G' for each cement at different concentrations of SP2 with addition of limestone

	Initial value of *G'* x10^4 (Pa)			
Concentration of SP1, %	**C1**	**C2**	**C3**	**C4**
0	13	6.6	12.6	9.8
0.1	9.7	1.3	5.8	7.4
0.2	9.3	0.14	2.7	6.9
0.3	1.5	0.12	1.5	1
0.4	0.6	0.12	0.2	0.2
0.5	0.1	0.04	0.1	0.05
0.6	0.03	0.03	0.05	0.03

Considering the hydration time for all cements, C1 and C2 had the longest period of increasing *G'* value before reaching a plateau, followed by C4 and C3, respectively. Addition of limestone contributed to the decrease in the initial value of *G'* compared with the case of pure cement paste (Table 4.4).

Table 4-4: Initial value of *G'* for each cement with and without limestone

Initial value of *G'* x10^4 (Pa)		
Cement	**Cement without SP**	
	With LS	**Without LS**
C1	13	16.8
C2	6.6	10.9
C3	12.6	14.7
C4	9.8	10.2

In general, these results indicate that limestone delayed the hydration reaction of the cement paste. Taking the case of SP1 without limestone, the longest time to reach the plateau for SP1 without limestone was at 17 minutes, while with the addition of limestone there was a smaller range of values with the highest hydration time about 42 minutes.Cement paste with limestone and SP2

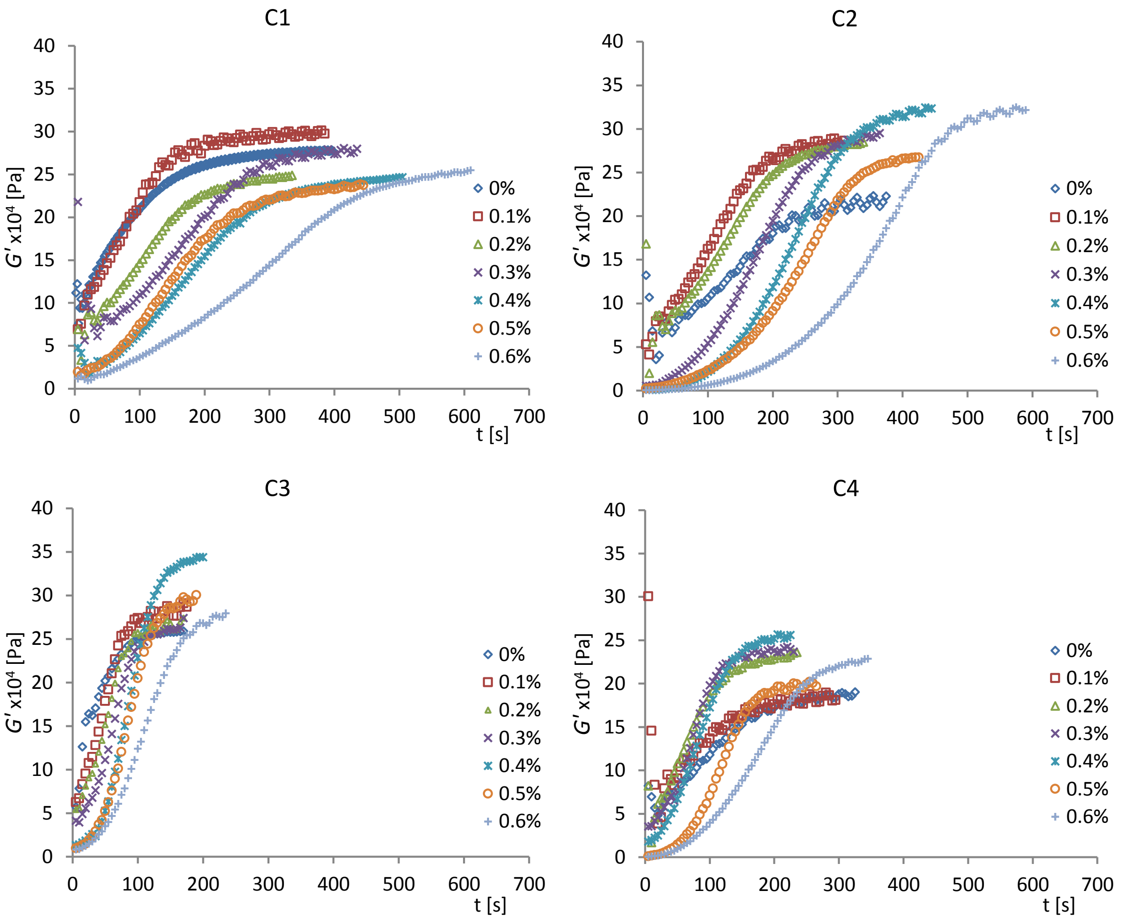

Figure 4-4: Elastic modulus evolution for the four cements with different concentrations of SP2 (0% - 0.6%) with addition of limestone

The influence of the different concentrations of SP2 (0% - 0.6%) on limestone cement pastes is given in Figure 4.4. As for SP1, increasing superplasticiser dosage corresponded to an increase in the duration of both the initial and dormant periods. However, the increases of the two periods were not uniform at the different dosages of SP2 for each of the cements.

The initial values of the elastic modulus for the four cements at different concentrations are presented in Table 4.5.

Table 4-5: Initial value of *G'* for each cement at different concentrations of SP2 with addition of limestone

Initial value of *G'* x10^4 (Pa)				
Concentration of SP2, %	**C1**	**C2**	**C3**	**C4**
0	13	6.6	12.6	9.8
0.1	11.9	4.1	11.4	8.3
0.2	8.0	2.0	9.5	4.5
0.3	7.1	0.5	6.8	4.2
0.4	2.7	0.2	2.6	2.2
0.5	2.4	0.2	2.3	0.2
0.6	1.3	0.04	1.7	0.1

Figure 4.4 data shows that C1 and C2 had the longest time before reaching the plateau, followed by C4 and C3. It was also noted that when SP2 was used without the addition of limestone, the hydration reaction of the cements followed a different trend such that C1 and C4 presented the longest time, while C2 and C3 had the lowest times of hydration.In the absence of limestone, the time required to reach the plateau for SP2 (0.6%) was estimated at 7 minutes, while in the presence of limestone it was 12 minutes, indicating that limestone delayed the hydration reaction of the cement paste. This was similar for both SP1 and SP2. These results are discussed in the subsequent section which reports on the effects of cement properties, superplasticiser concentrations and limestone dosage on the hydration reaction of self-compacting concrete paste (SCCP).

4.3 Hydration kinetics

Elastic modulus evolution

The main objective of this research was to investigate the initial hydration reaction mechanism of the cement paste with different concentrations of superplasticiser with this intent of leading to the selection of a self-acceleration equation that adequately fits the cement paste hydration reaction process.Observing the evolution of the elastic modulus of the four cements with and without limestone and with the addition of SP at different concentrations, a kinetic equation of self-acceleration type is proposed to predict this behaviour.

The rheokinetic modelling for the self-acceleration, obtained from polymer science (Malkin & Kulichikhin, 1996), was used to describe the initial hydration of the self-compacting concrete paste for the first time. From this equation, three main variables were defined, namely self-acceleration constant, characteristic time and real time of hydration.

The observations apparent in Figures 4.1, 4.2, 4.3 and 4.4 demonstrate that the hydration mechanism and the resulting elastic modulus values are time-dependent.

$$\frac{d\beta}{dt} = \frac{1}{\theta}(1-\beta)(1+K\beta), \qquad 4.1$$

where β is the measure of the chemical transformation; Θ is the characteristic time constant determining the starting rate equal to Θ^{-1}; K is a dimensionless parameter reflecting the rate of self-acceleration; and t is the time.The integral of Equation 4.1 can be presented as:

$$\frac{1}{1+K}[-ln(1-\beta) + ln(1+K\beta)] = \frac{t}{\theta} \qquad 4.2$$

From Equation 4.2 it can be seen that at $t = 0$, $\beta = 0$. In order to determine the parameters of kinetic laws for each of the cements, it is necessary to find the optimal fitting of K and β with the experimental data. K can be found at the point where the reaction rate is at its maximum, meaning using the value of βm at which $d^2\beta/dt^2 = 0$. At this point:

$$K = \frac{1}{1-2\beta_m} \qquad 4.3$$

The value of Θ can then be determined from the slope of the curve at the beginning of the hydration or can be estimated analytically by selecting two corresponding values for t and β at the beginning or toward the middle of the curve. From the experimental values of elastic modulus, β is written as:

$$\beta(t) = \frac{G(t) - G_0}{G_\infty - G_0} \qquad 4.4$$

When assuming that the initial elastic modulus Go is zero, β can be estimated as the ratio of the elastic modulus $G(t)$ at given time (t) and elastic modulus at the plateau end of the curve G_∞. The calculations of Equation 4.1 help in estimating the rigidification time (T^*) of cement paste by assuming that T^* corresponds to $\beta = 0.95$.

$$T^* \cong \frac{\theta}{1+K}[3 + ln(1+K)] \quad 4.5$$

The constant ‘3’’ in Equation 4.5 is a result of assuming the final degree of conversion to be equal to 0.95.The focus on cement rigidification turns towards the investigation of the two kinetic constants *Ɵ* and *K. Ɵ* characterises the duration of the dormant period, while *K* is the rate of self-acceleration constant which determines the final part of the kinetic curve. The dependency of these constants on the cement paste helps us understand the mechanism of hydration process and the effect of cement properties, superplasticiser (type and dosage) and limestone dosage on hydration of cement paste.The rate of the reaction for the four cements was determined by the following equation:

$$R_h = (1-\beta)(1+K), \quad 4.6$$

where *R*h could conventionally be called the relative rate of hydration or the speed of the reaction. Thus *R*h depends on the value of *K*. From the experimental results, the following coefficients of the rheokinetic model were discussed according to SP used in the presence and absence of LS.Cements paste with SP1 without LS

Self-acceleration constant (K)

Figure 4.5 shows that self-acceleration values increased with increasing SP dosage for all cements and same with time of hydration. However, the increase in self-acceleration constant was not uniform for the four cements at similar SP dosages.

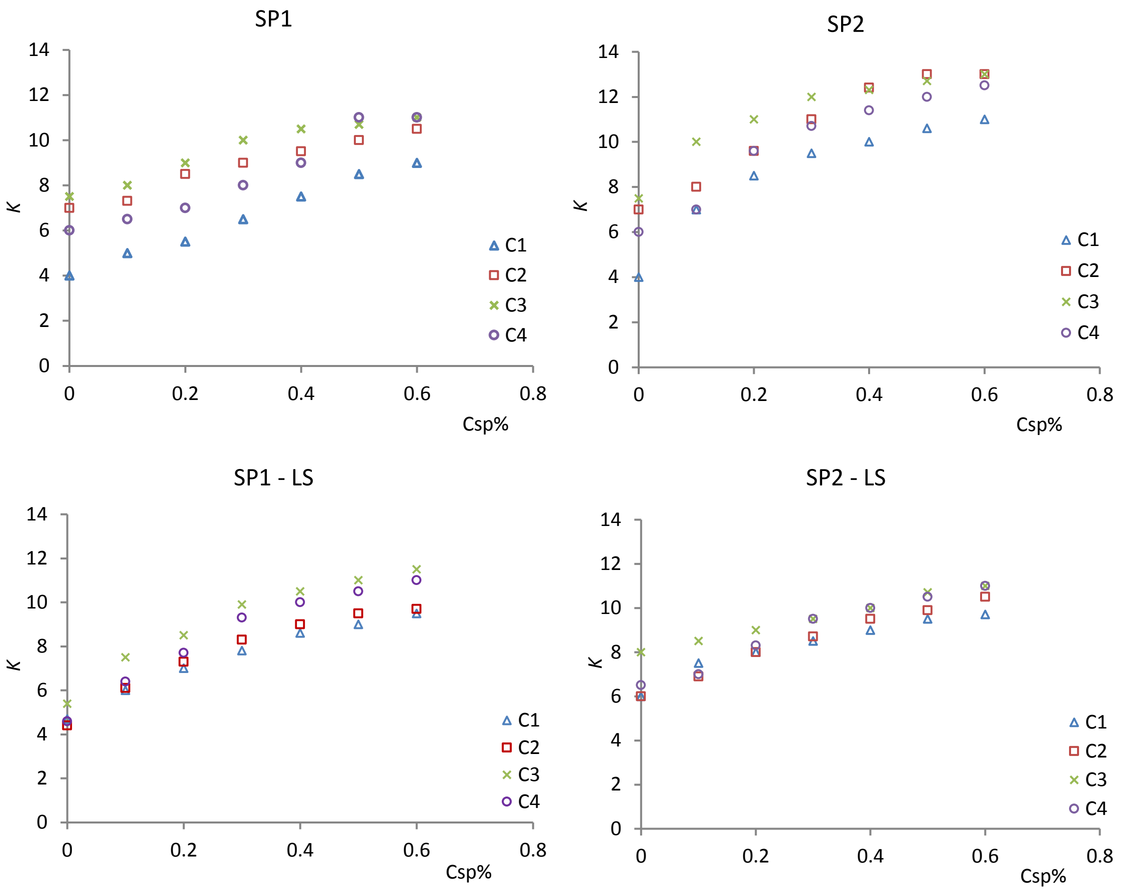

Figure 4-5: Self-acceleration kinetics of SP1 & SP2 (with and without limestone)

The four cements displayed a faster increase in the kinetics when the superplasticiser dosage was increased from 0% to 0.3%. At a concentration higher than 0.3%, there was a lower increase in self-acceleration kinetics with a further increase in superplasticiser for all cements. Cement C3 displayed the greatest value of *K* while C1 displayed the lowest *K* value at all superplasticiser dosage values for all cases (SP1, SP2, SP1-LS and SP2-LS). Generally, the use of SP2 resulted in higher *K* values as compared to SP1 for all the cements, while the highest value of *K* for SP1 and SP2 were close, being estimated at 11 and 13 respectively for C3 cement.

The second focus was on determining what effect the use of limestone would have on hydration reaction. Again, different self-acceleration constant values were observed for the same cements with the addition of limestone.Figure 4.5 data shows that the use of limestone decreased the self-acceleration, regardless of the type of superplasticiser used.

With SP2 a different trend was observed with the addition of limestone. When using SP2 without limestone, the self-acceleration values were the lowest for C1 and increased through C4, C2 and C3, while with the addition of limestone, C1 and C2 had the lowest self-acceleration values, followed by C4 and C3.

With the addition of limestone, the use of SP1 resulted in lower hydration reaction compared to SP2 for all the cements. It could be seen that when SP dosage was increased, the *K* value increased as well and so the *R*h maximum shifted towards the right side of the hydration time (Figure 4.6). This would be an indication that the rate of hydration slowed when *R*h or *K* increased.

The relative rate of hydration (R_h)

Figure 4.6 shows the changes in speed of reaction from the initial increase up to a maximum, followed by a progressive decrease until the completion of the reaction. The effect of superplasticiser on the speed of hydration can also be seen from graphs in Figure 4.6. An increase in superplasticiser concentration was shown to decrease the speed of the hydration reaction, thereby increasing the time required for the reaction to come to completion. However, it was also seen that the value of the maximum speed achieved in the reaction increased with increasing superplasticiser concentration, but due to the delay in hydration reaction, the time required to reach maximum speed increased with increasing superplasticiser concentration. This can be explained as the superplasticiser initially delayed the reaction, but once the reaction proceeded, it reached the maximum relative rate of hydration *(R*h*)* value before starting to decrease.

Reduction of *R*h curves to the same first point removes the effect of the initial rate of the reaction and more clearly presents the self-acceleration role, as shown in Figure 4.6.

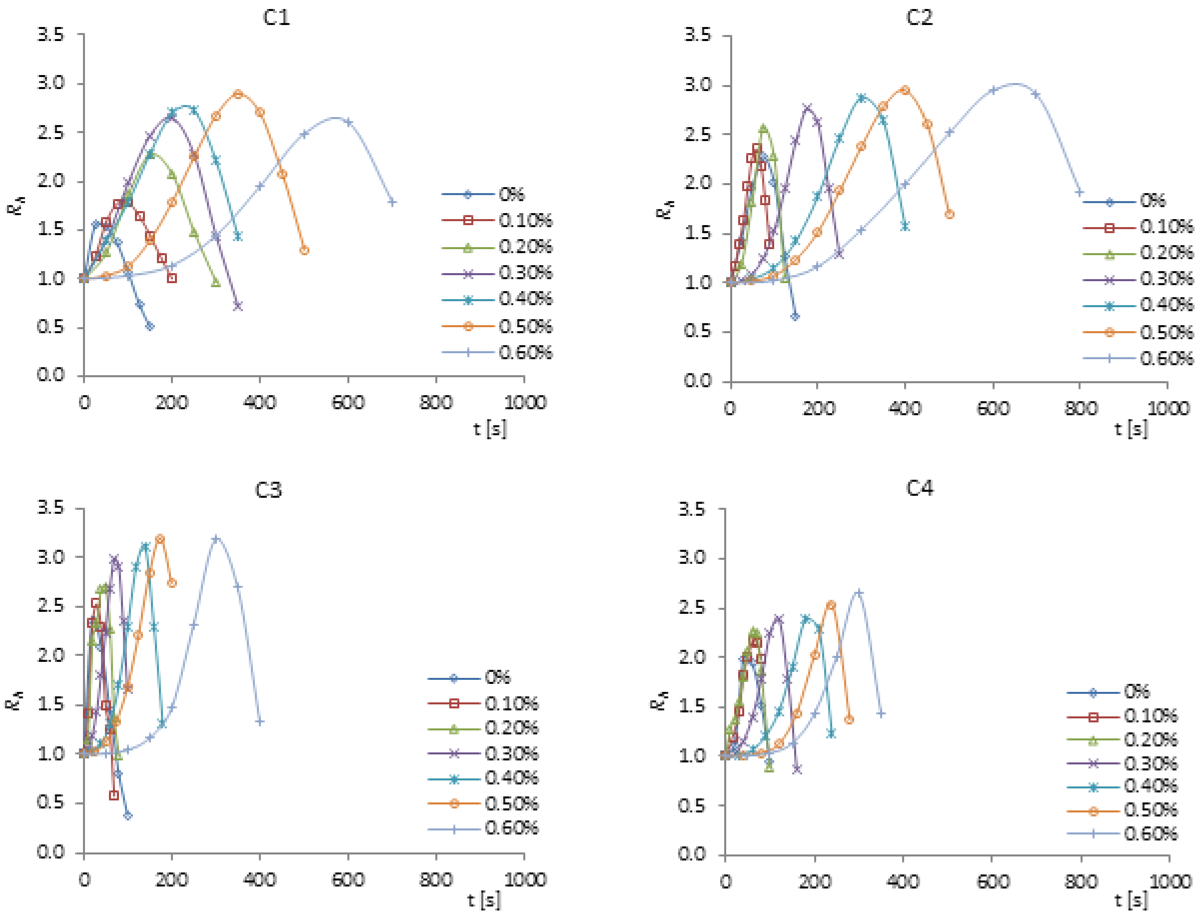

Figure 4-6: Effect of SP1 on the kinetic model curve (without limestone)

All other relative rates of hydration or speed of the reaction curves obtained from the samples under study were similar.

Characteristic time (ϴ)

Characteristic time which corresponds to the total time of the reaction within the material, meaning the reaction is proceeding at the same rate, was analysed in Figure 4.7.

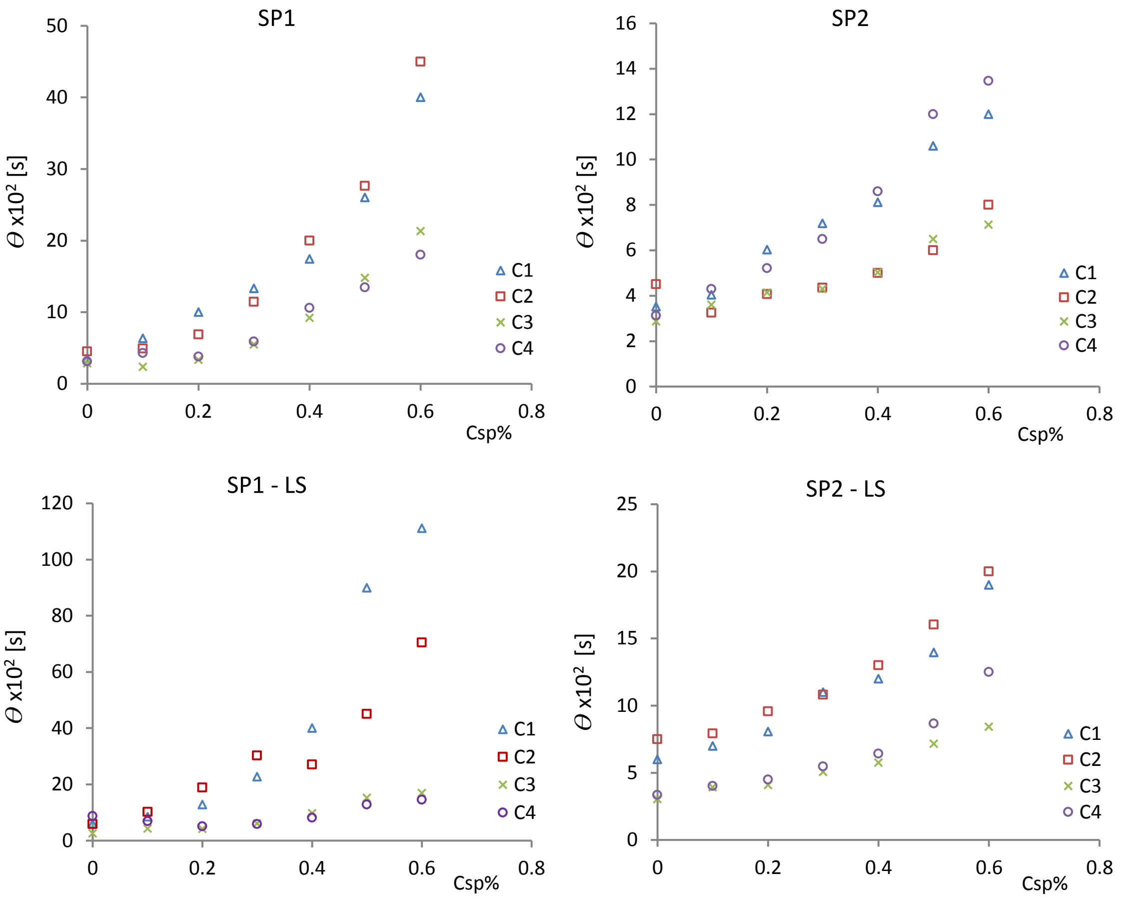

Figure 4-7: Characteristic time curves of SP1 & SP2 (with and without limestone)

At low superplasticiser concentrations between 0% and 0.3%, there were no major differences between the values of the characteristic time. However, at concentrations above 0.3% major discrepancies appeared.For SP1 with and without LS, C1 and C2 reached the highest values and C3 and C4 had the lowest characteristic time values (Figure 4.7). In the case of SP2 without LS, C1 and C4 displayed the greatest values of characteristic time, while C2 and C3 had the lowest characteristic time values at all superplasticiser dosage values. The presence of limestone changed the trend from C1 and C2 followed by C4 and then C3.This behaviour linked properly with the previous observations concerning the rate of hydration of cements in Figures 4.1 - 4.4. It is clear that cement with a low rate of hydration would result in long characteristic time, indicating the length of its hydration time.Figure 4.7 shows that the use of SP1 exhibited a higher characteristic time as compared to SP2 for the four cements. The highest characteristic time for SP1 was recorded for C2 and was estimated by extrapolation at about 75 minutes, or more than an hour, assuming there were no other reactions taking place. This could be different if other reactions had occurred. In the case of SP2, the highest characteristic time was recorded for C4 and was estimated at 23 minutes.The addition of limestone contributed to an increase in the characteristic time values as compared to the case of cement without limestone.

The real time (T)*

The real time is the actual time the elastic modulus takes to reach the plateau that defines the chemical equilibrium within the cement paste. The trends of real time are generally similar to those of characteristic time but with small differences.

Just as in the case of characteristic time, the real time value increased slowly for superplasticiser value up to 0.3%; however, a rapid increase was observed when the superplasticiser value exceeded 0.3, as seen in Figure 4.8 where superplasticiser values between 0.3 and 0.6% were used.

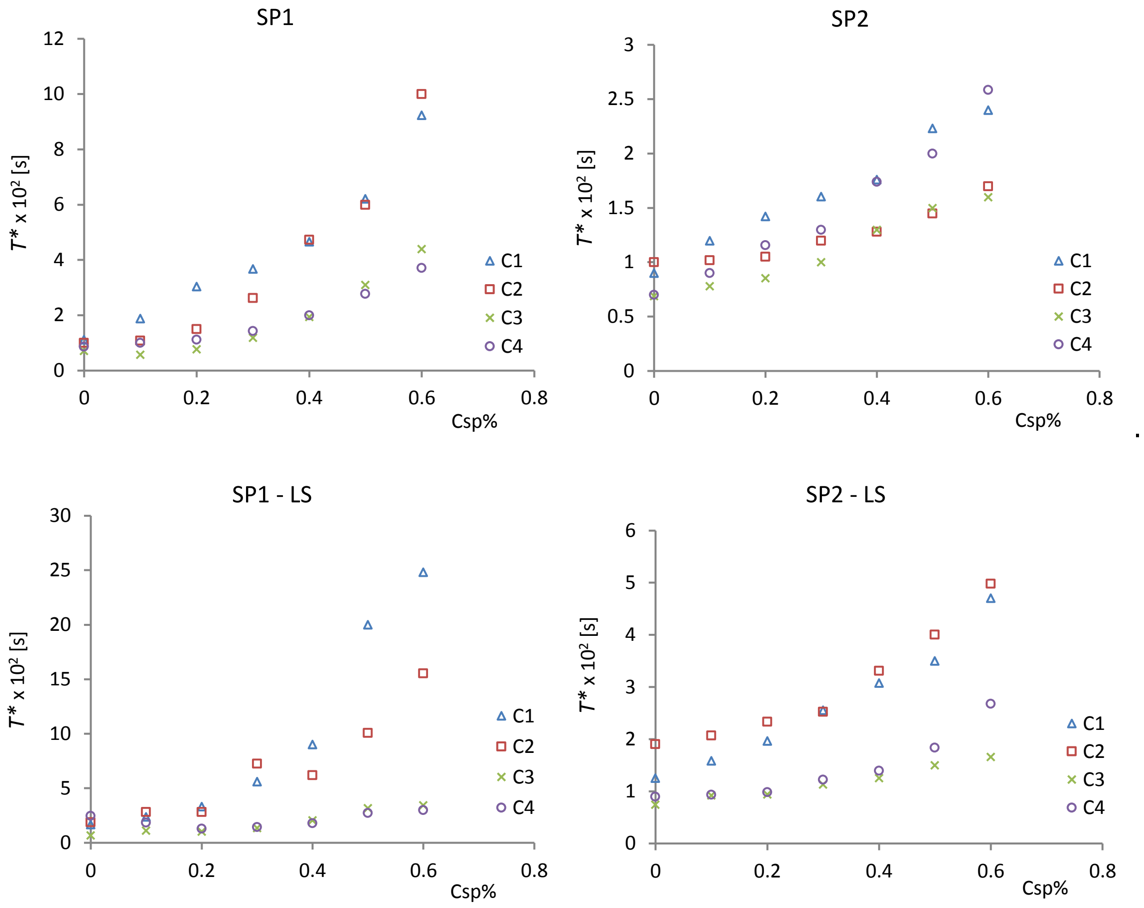

Figure 4-8: Real time curves of SP1 & SP2 (with and without limestone)

In all cases, C1 and C2 displayed the greatest value of real time, while C3 and C4 displayed the lowest real time value at the higher superplasticiser dosage values, except when using SP2 without LS. In that case, C1 and C4 displayed a faster increase in the real time when the superplasticiser dosage was increased. C2 and C3 only experienced a slight increase with increasing superplasticiser dosage. A comparison of result obtained using SP1 and SP2 reveal that the use of SP1 resulted in a more retarded hydration as compared to SP2. The use of limestone also resulted in a more retarded hydration.

4.4 Effect of cement characteristic, limestone and superplasticiser on the rheokinetics of cement paste

Considering the above, it is clear how the rate of hydration kinetics is very important to the rigidification process of cement paste.Firstly, the difference in rheological behaviour of the cements could be depicted by the established rheokinetic coefficients such as self-acceleration constant, characteristic time, relative rate of hydration and real time. Secondly, these disparities were attributed to both physical and chemical properties of cements.

Previous studies conducted separately by Michaux *et al*. (1989) and Vikan (2005) concluded that during early hydration, C_3A has a stronger influence on the rheological properties of the cement paste, while other cement compounds such as C_3S have a higher impact at later stages. In fact, C_3A has a higher reactivity as compared to the other cement compounds. For this reason, the rheological behaviour of cement paste is assumed to be affected mostly by the hydration of C_3A cement phase in the early stage.

Effect of superplasticiser type on the hydration

The interactions between cement and superplasticiser are known to influence the flow properties of the cement paste. From the results obtained in this work, generally speaking, the addition of SP in the mixtures somewhat retards the hydration reaction, regardless of the dosage and SP type used. According to Puertas *et al.* (2005), Zhang and Kong (2015) and Lange and Plank (2016), SP is adsorbed on C_3A particles, coating its surfaces, and by steric hindrance effect repulses adjacent particles. Trapped water between particles therefore improves the workability. This repulsion ability of SP depends on the type of superplasticiser used and on a few other cement properties such as alkali content in the clinker, cement fineness and calcium sulphate content.

In the case of SP1, the retardation effect is illustrated in Figure 4.6, showing that SP1 prolongs the hydration process of the four cements. C1 and C2 presented the highest characteristic time Θ followed by C3 and C4. Cements with high C_3A and alkali content resulted in low hydration rate, as for cement C1 (3.95, 0.75) and cement C2 (2.75, 0.41). Cements C3 (1.84, 0.29) and C4 (2.63, 0.33) had low C_3A and alkali content which thus resulted in a high hydration rate that affected their hydration time. These results are in agreement with a previous study conducted by Bellotto (2013) who found that the rate of hydration increased with increasing C_3A content in the absence of SP.

With the addition of SP2, cements behaved completely differently as compared to their rheokinetics behaviour when in the presence of SP1. In this case, the hydration rate was the lowest for C1 and increased through C4, C2 and C3 successively. The presence of sulphate alkali (K_2SO_4) in the cements was found to be the cause of this rheological behaviour. Table 3.2 shows the concentration of K_2SO_4 for each of the cements. In fact, according to Vikan *et al*. (2007), the interaction between cement and SP depends on SO_4^{2-} concentration in the solution. Arcanite or sulphate alkali (K_2SO_4) decreases the adsorption of SP on cement compounds during the initial hydration. This causes more SP to remain in the solution, thereby increasing the dispersion between cement particles and consequently the flowability of cement paste. It is of great importance, therefore, to consider the concentration of K_2SO_4 in a given cement when a polycarboxylate-based SP is used. The higher the K_2SO_4 content, the longer the hydration reaction. In particular, it was observed that with the addition of SP2 to the cement pastes, cements C1 and C4 exhibited the highest characteristic time while cements C2 and C3 presented the lowest values at all SP2 dosages.

Looking at the effect of SP concentration on the rheological behaviour of cements, results showed that an increase in SP dosage decreased the rate of the hydration reaction, subsequently increasing the time required for the reaction to come to completion, as demonstrated in Figures 4.7 and 4.8. Both the characteristic time and real time of each cement increased with increasing SP dosage. In a separate investigation by El-Gamal *et al.* (2012), an increase in superplasticiser concentration delayed the rate of cement hydration, potentially leading to retardation of initial and final setting times.

It was also important to assess the effectiveness of the two superplasticisers used with the objective of determining which one had more effect on the rheokinetics of cement paste during hydration. In general, it was found that the use of SP1 further retarded the hydration with high values of characteristic time compared to those obtained when SP2 was used. This effect can be attributed to their difference in alkali, Na_2O content (Table 4.6). The effect of the concentration of soluble alkali in the solution has been addressed by Vikan (2005). In addition, Wistuba *et al.* (2007) reported that Na_2O led to a delay in the formation of ettringite in the early stages of hydration, implying a delay of the reaction between the remaining C_3A and ettringite to yield more stable hydrates responsible for setting. This could explain the difference in hydration rates observed for the two superplasticiser types. It can also be suggested that SP1 would be better suited for applications where more time is required before the hardening of the paste.

Table 4-6: Na_2O content for SP1 & SP2

Alkali content (Na_2O equivalent) (%)	**SP1**	**SP2**
	<2.5	≤1.0

Effect of limestone on cement hydration

From the results, it can be observed that the addition of limestone in the cement paste with SP resulted in the lowest hydration rate. This was attributed to the interaction between SP, C_3A and sulphate that mostly affects the hydration time of cement paste.Similar results have been recorded by Moratti *et al*. (2012) in their recent investigations, as they confirmed that the use of polycarboxylate as superplasticiser leads to the retardation effect of cement hydration when blended with limestone.

A number of studies conducted by other scholars such as Lerch (1946), Michaux *et al.* (1989) and Ghorab *et al.* (2010) indicated that in the presence of sulphate, cement paste with a higher C_3A and alkali content exhibited a longer hydration time when compared to those with low C_3A content pastes. In particular, Lerch (1946) found that regardless of alkali content in the clinker, cements with higher C_3A content presented a low hydration rate due to the dissolution of sulphate and calcium ions which stem from the hydrolysis of various compounds (i.e. gypsum and lime in water). This lime-gypsum solution saturated the solution thereby depressing the solubility of alumina and consequently the hydration of C_3A. Lerch (1946) revealed that in the case of cements with both low C_3A and alkali content, the speed of their hydration in the presence of gypsum depends strongly on the formation of a crystalline hydrated calcium sulfoferrite which does not affect the hydration of C_3A phase. Hence, hydration occurs at a higher rate. This was also confirmed by Ghorab *et al.* (2010).

The adsorption of SP on the cement particles depends on the competition between C_3A and sulphate, as reported by Vikan *et al.* (2007) who found that for the initial hydration, sulphate is known to prevent the adsorption of SP on C_3A, resulting in more SP remaining in the suspension, and thus allowing the repulsion effect between cement particles. Consequently, the hydration of cement paste would take longer in the presence of gypsum (Ghorab *et al.,* 2010).

It was also noted that when limestone was used with SP, the hydration reaction depended on the C_3A content in cements. This can be explained by the fact that a higher amount of C_3A leads to a stronger reaction with $CaCO_3$ to form monocarbonate (Celik *et al.,* 2015). This hydrate has been reported in the literature as an agent that indirectly provides a high stabilisation of ettringite around cement particles (Lothenbach *et al.,* 2008; De Schutter, 2011; Matschei *et al.,* 2007). Ettringites stem from the reaction between C_3A and sulphate that precipitates on cement compounds and slows the hydration process.Cements with high C_3A content (Table 3.2) in the presence of SP and limestone therefore exhibited a low rate of hydration, while those with a low content of C_3A exhibited a rapid hydration rate, as presented in Figures 4.7 and 4.8.

Chapter 5. Conclusions

5.1 Introduction

Self-compacting concrete is a flowable concrete that is able to consolidate under its own weight. The performance of self-compacting concrete (SCC) is highly dependent on the rheological properties of self-compacting concrete paste (SCCP) systems.Cement varies considerably depending on the process and properties of the materials used. The effects of chemical admixtures and mineral fillers such as superplasticisers and limestone respectively, are of special technological interest, especially when dealing with self-compacting concrete (SCC). Their main purpose is to reduce the yield stress to improve flowability and generally also delay the hydration reaction.The hydration reaction occurs when water is added to cement. The hydration reaction of cement paste is complex and is effected by many factors. The variation in properties of cements which interact with other constituents results in a variety of reactions in the concrete mixture.

The equipment required for a proper collection of elastic modulus results was readily available in the laboratories of the Flow Process and Rheology Centre at the Cape Peninsula University of Technology, Cape Town, South Africa. An Anton Paar MCR-51 rotary viscometer was used in this research.The parallel plate attachment was used for all the elastic modulus measurement. The strain value was set at 0.2% and the value of the angular frequency was set at a constant value of 1 Hz. The gap between the two plates was set dependent on the particle size. The roughened parallel plate system was used for all measurements to reduce the possibility of slip. The temperature of the laboratory was maintained at 25 °C. The main aim of this work was to study the kinetics of hydration reaction of four cements of the same specification manufactured at different factories with and without the addition of two different superplasticisers and limestone to propose a general kinetic equation of the self-acceleration type for quantitatively describing the hydration process which could then be suitable for similar systems.

5.2 Summary

The rheological properties and hydration reaction of four cements (Ordinary Portland Cement) suspensions was investigated for two types of superplasticiser suspensions (each type considered separately) both with and without the addition of limestone. The kinetics of the hydration process can be described by different rheological parameters (viscometry and modulus measurements).Small amplitude oscillations in dynamic measurements were used to study the rheokinetic behaviour of cement paste during the early hydration. The findings revealed a rapid increase in *G'* values over time until these values became constant. The value of storage modulus at the beginning of this plateau was about 10^5 Pa. It was observed that cement paste hydration was more pronounced during the first minutes after the completion of the mixing. The rate of hydration varied considerably between the different cements depending on the type of superplasticiser used. The addition of limestone affected the hydration kinetics of cement pastes by extending the hydration times.

The data obtained from experiments were fitted using a rheokinetics model of self-acceleration type. From this equation, three main coefficients were defined – self-acceleration constant, characteristic time and real time of hydration – each of which aided in characterising the hydration process of individual cements in the presence or absence of limestone and SP. Each cement exhibited different rheological properties based on the values provided by the rheokinetics mode, differences related to variations in physical and chemical compositions of cements.In general, cements with high self-acceleration constant *(K)* and characteristic time *(Θ)* values resulted in a low hydration rate, whilst those with low values exhibited a high hydration rate. In particular, the presence of SP in cement pastes increased the characteristic time and the self-acceleration constant values during hydration. SP1 showed a greater effect on the rate of hydration than SP2 as the values of the self-acceleration coefficients of cement pastes with SP1 were higher than those with SP2.

The increase of SP concentration significantly affects the rate of hydration by increasing the hydration time of both blended and unblended limestone cement pastes. This was indicated by the initial delay observed in the evolution of the storage modulus.The addition of limestone to the cement paste with polycarboxylate SP decreased the rate of hydration by experiencing a long hydration time. Understanding the effect of limestone on the hydration kinetics of cement paste in the presence of polycarboxylate superplasticiser is significant since the development of the cement microstructure strength depends on hydration process.
In conclusion, the following can be stated:

- The rheokinetic equation of self-acceleration type could be used to characterise the hydration of blended cement paste.
- The hydration of the cement paste depends strongly on the chemical properties of the cement.
- Gypsum has an important role in controlling the hydration of C_3A.

- The factors affecting hydration mainly depend on the type of superplasticiser used. In the case of SP1, C_3A and alkali were the main factors but when SP2 was used, K_2SO_4 seemed to be the most influential factor affecting hydration.
- Superplasticiser retards the hydration of the cement paste, the effect being more significant for higher superplasticiser content.
- The superplasticisers with high content of Na_2O were more efficient in delaying the hydration process.
- The addition of limestone in cements with polycarboxylate acid-based SP drastically decreased the rate of hydration.
- The effect of limestone on the hydration time of cement paste was attributed to the interaction between SP, C_3A and sulphate content in the cement under investigation.

5.3 Contribuition

The main contribution of this research is that this project validates the possibility of using the described rheokinetics model to study the hydration of cementitious materials (i.e. cement blended with mineral and chemical admixtures). The understanding of the hydration of cementitious materials is crucial for transport, pumping, placing, curing and quality control of concrete or mortar.The findings of this research have been published in *The Applied Rheology Journal*:Elmakki, R., Masalova, I., Haldenwang, R., Malkin, A. and Mbasha, W. Effect of limestone on the cement paste hydration in the presence of polycarboxylate superplasticiser. Applied Rheology, DOI:10.3933/ApplRheol-26-25122.

5.4 Recommendation

The findings of this research revealed that more could and should be done to more thoroughly understand the interaction of cement and admixtures used during hydration. It is suggested that a future in-depth study quantify the effect of each cement compound identified on the hydration of limestone blended cement. In addition, the effectiveness of this rheokinetics model could be validated by using other supplementary cementitious materials such as fly ash or slag, and its accuracy verified by comparing the rheokinetics behaviour obtained to those predicted by other available models.

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Appendices

Appendix A. Speed of hydration of the cement

Cement paste without limestone – SP1

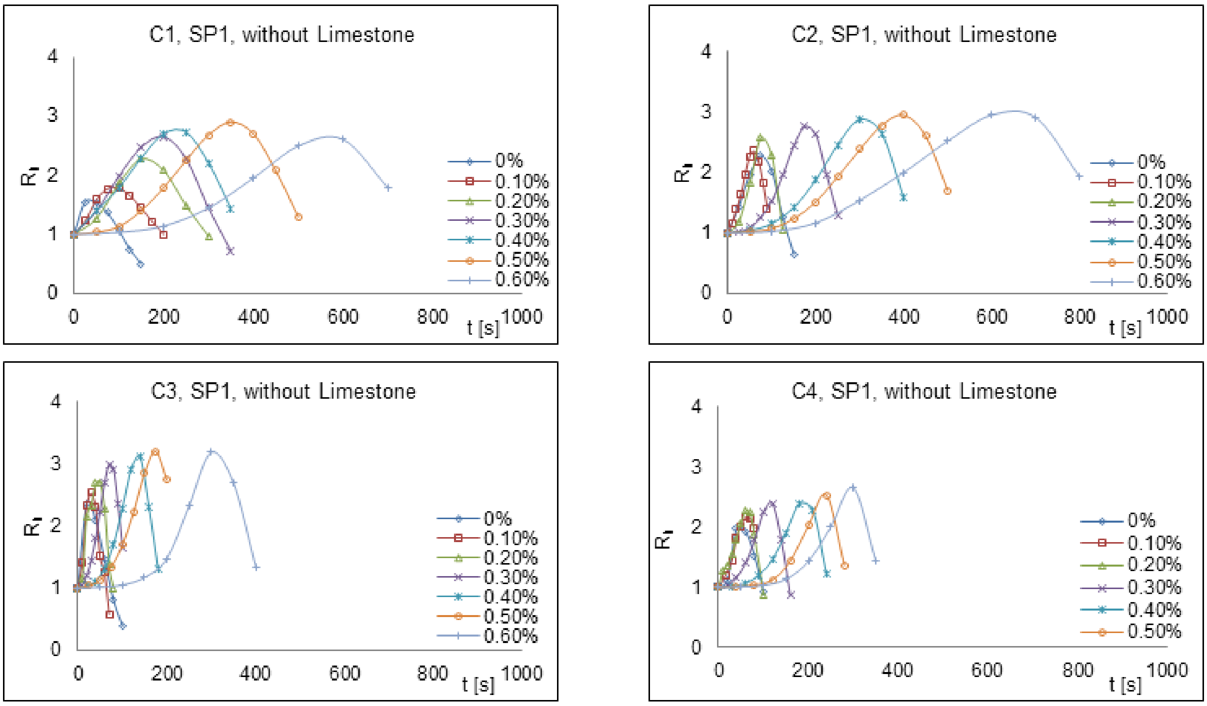

Figure A-1: Influence of the superplasticiser concentration on the rate of hydration for the four cements with superplasticiser SP1: 0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, and 0.6%

Cement paste without limestone – SP2

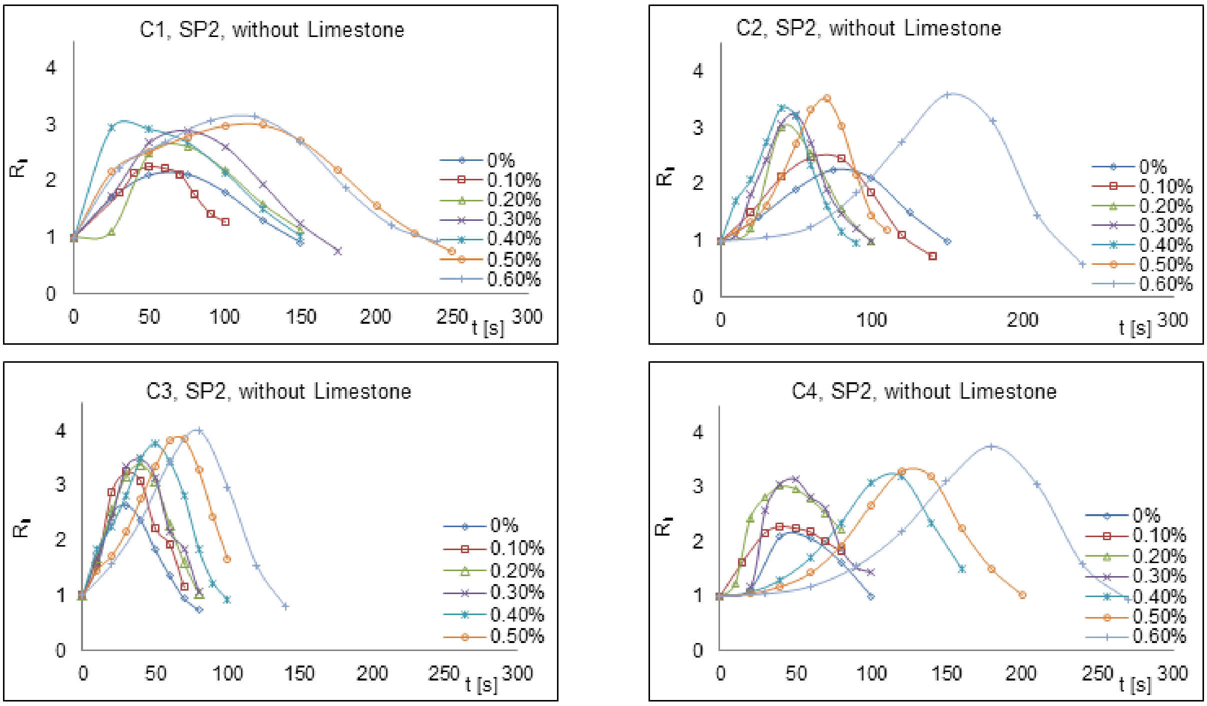

Figure A-2: Influence of the superplasticiser concentration on the rate of hydration for the four cements with superplasticiser SP2: 0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, and 0.6%

Cement paste with limestone – SP1

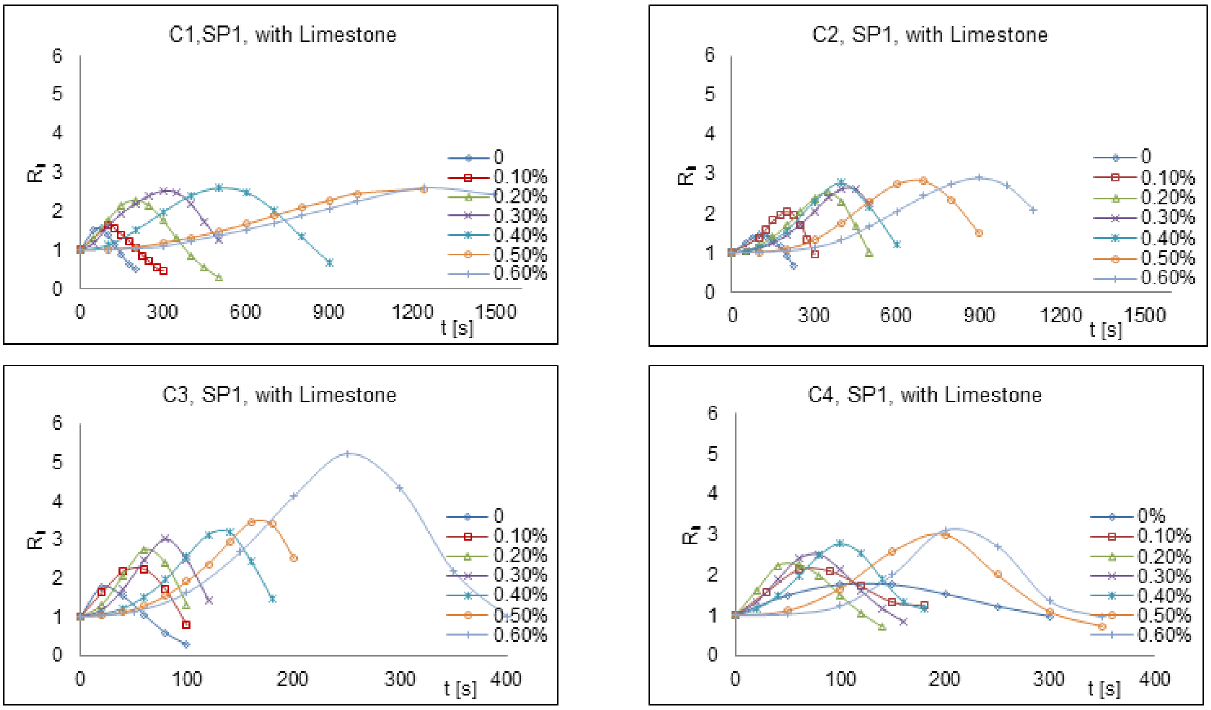

Figure A-3: Influence of the superplasticiser concentration on the rate of hydration for the four cements with limestone and superplasticiser SP1: 0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, and 0.6%

Cement paste with limestone – SP2

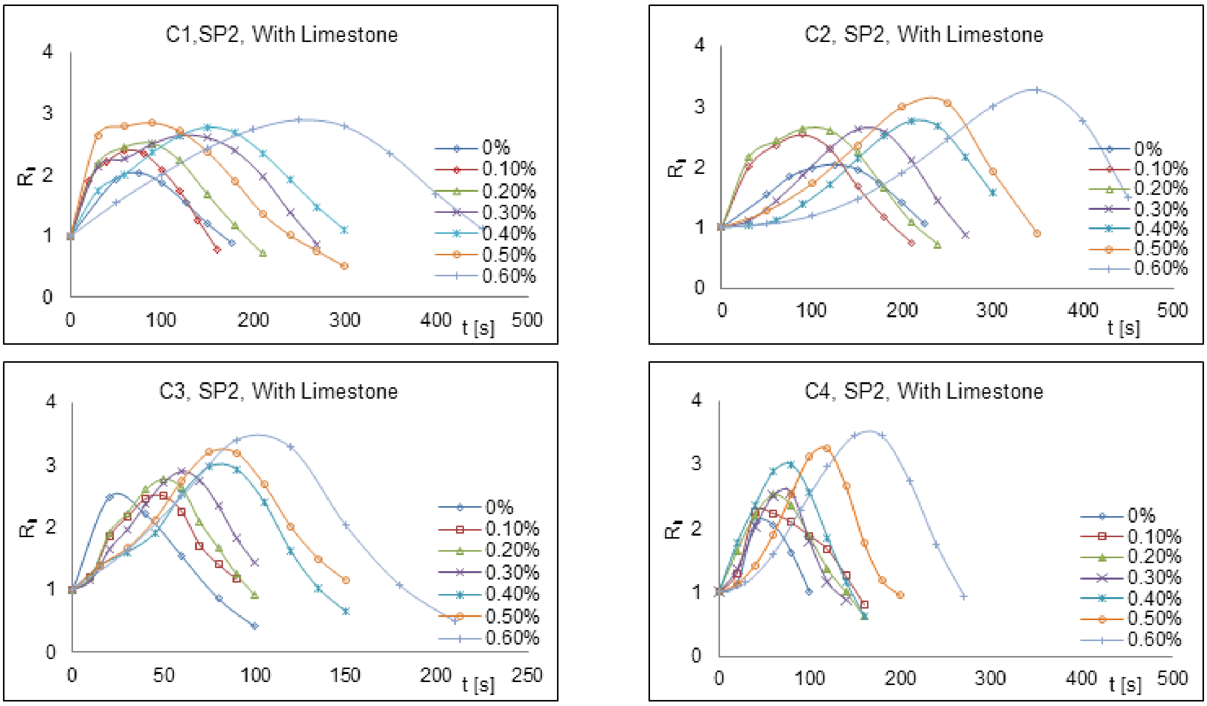

Figure A-4: Influence of the superplasticiser concentration on the rate of hydration for the four cements with limestone and superplasticiser SP2: 0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, and 0.6%