THE EFFECT OF PORTLAND CEMENTS AND SUPERPLASTICISERS ON THE RHEOLOGY OF CEMENT PASTE

by

WILLY MBASHA MIGABO
B.Tech: Civil Engineering, (Structural)

Dissertation submitted in partial fulfilment of the requirements for the degree

MTech Degree in Civil Engineering

in the Faculty of Engineering

at the Cape Peninsula University of Technology

Cape Town
1 July 2015

Declaration

I, WILLY MBASHA MIGABO, declare that the contents of this dissertation represent my own unaided work. It is being submitted for the MTech Degree at the Cape Peninsula University of Technology, Cape Town. It has not been submitted previously for any degree or examination at this or any other university.

____

(signature)

Signed in Cape Town, this ______________ day of _________________ 2015

Abstract

Self-compacting concrete is very sensitive to variation in cement properties and to the interaction between cement paste and additives such as superplasticisers. The assessment of these interactions can be done rheologically but there is as yet no consensus on how to evaluate the rheological properties (yield stress and viscosity) of cementitious materials. In addition, there is no clear understanding of the dependency of these rheological properties on early hydration, evaluations which are recommended to be done at paste scale.

The evolution of rheological parameters in the early stage of hydration, of four CEM I 52.5N cements manufactured at different factories in South Africa, and their interaction with two different commercial superplasticisers (SPs) were investigated using three different rheometric techniques: conventional flow curve from hysteresis loops, amplitude sweep in oscillation mode and construction of flow curve.

Amplitude sweep, time sweep, viscosity-time sweep as well as thixotropy tests were conducted to investigate the effect of hydration and the rate of rebuilding of each cement in the presence and absence of SP. The experiments were done on a MCR51 rheometer with roughened parallel plates under controlled temperatures and relative humidity.

Results show that yield stress values from constructing the flow curve, as well as those from amplitude sweep, could be used to characterise the rheological behaviour of cement paste, instead of conventional flow curve from hysteresis loop that provided yield stress values which could not provide more information about the change in cement paste microstructure. Coefficients of the developed rheokinetic model described well the kinetics of cement hydration and could be linked to the flow properties of cement paste.

Though all cements were the same type CEM I 52.5N, their individual rheological behaviour was very specific, differing one to the other. The difference in their flow behaviour was attributed to the interaction of their chemical composition during the hydration process. The alkali equivalent content in early hydration of cements with no addition of SP would be responsible for cement paste yield stress development, while the plastic viscosity behaviour was due to the gypsum content in cement. With the addition of SP, the competition between the concentration of SO_3 and C_3A was observed, governing the yield stress changes within cement pastes, whereas K_2SO_4 as well as Ca^+ ions available in C_3A phase were found to be the cause of cement paste fluidity loss.

The rate of rebuilding of these cement pastes depended strongly on the hydration of C_3A, especially the cC_3A formation, K_2SO_4 and Na_2O within cements.

I can do all this through him who gives me strength.

Philippians 4:13

Dedication

To my dearest parents: Innocent Mbasha Muhamiriza and Sophie Cizungu Rhulinabo
To Patrice Kasigwa Nyenyezi and Marthe Cizungu Tabu
To Reverand Pere Rene-Robert Chofi Muhigirwa

Acknowledgements

I would like to express my utmost gratitude to my advisors, **Professor Rainer Haldenwang** and **Professor Irina Masalova,** for their guidance throughout my Master's degree studies at the Cape Peninsula University of Technology. Their insightful advice has been absolutely priceless and I am very fortunate to have them as mentors.

I would also like to thank **Professor Veruscha Fester** and **Mr Nazeem George** for technical assistance during the course of this project.

I would like to express my sincerest gratitude to **Madam Myriam Boeglin** and **Maria Mater Misericordae Foundation** for supporting my studies.

I thank my friends **Dr Mahabubur Rahman Chowdhury Fahaad**, **Shearna J. Brown**, **John Shamu Tafadzwa** and **Omar Almuwbber** for their encouragement and support in my hardest times. I appreciate everything they have done for me.

Most importantly, I must express my deepest gratitude to **PPC Cement** for supporting this project, both financially and technically.

Table of Contents

List of figures

In Appendices

List of tables

Nomenclature

Constants

A	Area of the upper plate
d	Relative reactivity
F	Force applied on the plate
g	Gravitational constant
h	Characteristic height
k	Consistency
K	Rate of self-acceleration
k_1	Empirical constant for calculating the strength of harden concrete
k_2	Empirical constant for calculating the strength of harden concrete
n	Power law index
R_h	Relative rate of hydration
T	Characteristic time of the deformation process
T^*	Real time or total time of regidification
t	Characteristic time of the material
t^*	Time
v	Shear velocity
x	Shape of the particle
y	Thickness of the liquid

Greek letters

η	Viscosity
$\dot{\gamma}$	Shear rate
η_c	Viscosity of the medium
η_p	Plastic viscosity
η_y	Viscosity at infinite
η_{pl}	Plastic viscosity at low shear rate
η_{pm}	Plastic viscosity at medium shear rate
φ_m	Maximum packing density
γ	Strain
θ	Characteristic time
α	Critical angle
δ	Phase shift

τ	Shear stress
ω	Angular velocity
ρ	Density of the paste
φ	Packing density

Terms and concepts

ΔE	Incremental potential energy
Admixture	Substance other than aggregate, cement or water added in small quantities to the concrete mix to alter its properties
Apparent viscosity	The shear stress divided by the rate of shear when this quotient is dependent on the rate of shear
AR	Aluminate ratio
AS	Amplitude sweep
Blaine	Surface area based parameter of cement particles
Bleeding	Separation of clear water from the cement paste of mortar or concrete
C	Cement
Clinker	Product of fusing together clay and limestone as the first stage in the manufacture of Portland cement
Coagulation	Sticking together of particles without their merging
C-S-H	Calcium silicate hydrate
C_{SP}	Concentration of SP
CSR	Control shear rate
CSS	Control shear stress
Deborah number	The ratio of characteristic relaxation time of a material to the duration of the observation
Deformation	A change of shape or volume or both
Elasticity	A conservative property in which part of the mechanical energy used to produce deformation is stored in the material and recovered on release of
fc	Compressive strength
Flow	A deformation, of which at least part is not recoverable
Flow curve	A graphical representation of the behaviour of flowing materials in which shear stress is related to shear rate
Flocculate	To cause to aggregate into flocculent

Flowability	Property of fresh concrete, mortar or cement paste describing their ability to flow
Fresh	Refers to cement paste or concrete that has been recently mixed and is still fluid
G’	Storage modulus
G”	Loss modulus
HSPC	High strength performance concrete
HRWRA	High range water reducer admixture
Hydration	The combination of water with any substance such as lime or minerals, which is responsible for the alteration of minerals in weathering; the formation of hydrated lime; the setting of cement, and so on
Kinetics	The study of reaction rates and the factors that affect them
Laminar flow	Flow without turbulence
LF	Lime factor
LVD	Linear viscoelastic domain
LSF	Lime saturation factor
Model	An idealised relationship of rheological behaviour expressible in mathematical, mechanical or electrical terms
Mortar	A mixture of sand, gravel, and rocks held together by cement paste
OPC	Ordinary Portland cement
Paste	A mixture of cement and water
PSD	Particle size distribution
Rheology	Science of the deformation and flow of matter
Rheometer	Device used for the measurement of rheological properties over varied and extended range of conditions
SCC	Self-compacting concrete
SCCP	Self-compacting cement paste
Setting	The transition from fresh cement paste to hardened cement paste
Setting time	Length of time that cement paste, mortar or concrete will set, harden or cure
Shear rate	The rate of change of shear strain with time
Shear stress	The component of stress that causes successive parallel layers of material body to move, in their own planes relative to each other
Shear thickening	An increase in viscosity with increasing shear rate during steady shear flow
Shear thinning	Differential viscosity decreases continuously with shear rate
Slump	A measure of consistency of fresh mixed concrete, mortar equal to the subsidence measured to the nearest 5mm of the moulded specimen after removal of the slump cone

Steady shear flow	Condition under which a fluid is sheared continuously in one direction during the duration of a rheometric experiment
Strain	The measurement of deformation relative to a reference configuration of length, area or volume, also called relative deformation
SP	Superplasticiser
SR	Shear rate
SSA	Specific surface area
Thixotropy	A reversible time dependent decrease in viscosity at a particular shear rate
V_A	Attractive energy
Viscoelastic	A time dependent property in which a material under stress produces both a viscous and elastic response
Viscous	The tendency of a liquid to resist flow as a result of internal friction.
Viscosity	The property of a material to resist deformation increasingly with increasing rate of deformation
VMA	Viscosity modifier admixture
V_{max}	Maximum energy
V_R	Repulsive energy
V_T	Total energy
w/c	Water cement ratio
Workability	Property of fresh concrete or mortar that determines the ease and homogeneity with which it can be mixed, placed, consolidated and finished
Yield stress	A critical shear stress value below which an ideal plastic or viscoelastic material behaves like a solid; above this value, plastic material yields while viscoelastic material flows like liquid

Chapter 1 Introduction

Concrete is an essential material used in the construction industry worldwide. Due to its high demand, concrete has become the second most consumed substance after water on this planet, to a point where many cannot conceive of a world without this material. Special attention has been paid to this sustainable building material in an effort to reduce any detrimental impact on the environment. This has been achieved by improving different techniques in the manufacturing process, and revising specifications that guide its design and regulate its placement. Moreover, innovation in both the cement and concrete sectors has resulted in the implementation of different concrete products such as high strength performance concrete (HSPC) and self-compacting concrete (SCC), both of which have played a major role in the promotion of this construction material throughout the world.

1.1 Background and motivation

Cement properties vary according to their mineralogy and are affected by the manufacturing process. It is therefore possible to have the same type of cements, but with different properties. In general, the performance of a concrete in terms of its workability and durability depends strongly on physical and chemical properties of cement used during the manufacturing. Thus, an understanding and knowledge of cement characteristics is key to achieving a concrete with specific properties (De Oliviera *et al.*, 2013). Self-compacting concrete (SCC) as defined by Sheinn (2007) is concrete that exhibits the ability to flow under its own weight and completely fills formwork, even in the presence of dense reinforcement. This type of concrete does not need any vibration and remains homogeneous during placement.

The flow behaviour and the performance of SCC are controlled by the properties of the cement paste (Nunes *et al.,* 2011). These properties are enhanced by mineral or chemical admixtures in order to obtain optimum flow. However, the interaction of these admixtures and cement can cause major problems such as segregation, bleeding and poor workability. It is therefore of great importance to assess experimentally the effectiveness of any SCC mix design. Generally, SCC testing experiments are carried out at concrete scale. However, at paste scale, this is not only easier to investigate, but more convenient, since most of the admixtures incorporated in SCC affect the cement paste (López *et al*., 2009).

Tattersall and Banfill (1983) define *rheology* as the science of deformation and flow of matter, establishing relationship between force, deformation and time. Cement paste is a colloidal material; its flow is simulated to that of non-Newtonian liquid and generally characterised by the

Bingham model. This model allows a simultaneous determination of the two important rheological parameters of cement paste, namely yield stress and viscosity (Neophytou *et al.*, 2010).

As far as flow is concerned, rheology is the best tool for characterising the flow behaviour of cement paste.

1.1.1 Self-compacting concrete in construction

There are some difficulties encountered in construction when using conventional concrete, problems which are directly related to the cost involved during concrete placement with dense reinforcing, complex formwork, and environmental and structural issues. To remedy these issues, a new composite material, with the ability to respond to these difficulties encountered in industry with the usage of conventional concrete, was developed by researchers in Japan (Okamura & Ouchi, 2003; Koehler, 2007).

Self-compacting concrete has been proven to be an effective material that can lessen the effect of some of these issues with concrete. In fact, SCC also has the ability to achieve consolidation without any use of vibrators. Besides its physical properties, SCC offers to the construction industry additional advantages in terms of cost, casting, site management and environmental benefits (Shi *et al.,* 2015; Walraven, 2003).

1.1.2 Self-compacting cement paste

The mechanical strength of concrete structures made from SCC depends on the stability of the fresh SCC. This stability is directly affected by phenomena such as bleeding, settlement and segregation which occur mostly on site during placement, either individually or simultaneously. However, segregation is the most complex. When it occurs during placement, it is called *dynamic segregation* and afterward during the dormant phase, due to sedimentation of coarse aggregates under the gravity force, it is called *static segregation*. Not much is known about the latter phenomenon as little attention has been paid to it (Schwartzentruber *et al*., 2006).

The two important characteristics of SCC – flowability and resistance to segregation – are related to the rheological parameters i.e. yield stress and viscosity. An understanding of these relationships is very important (Wallevik, 2003).

The flowability and stability of SCC is achieved by the use of different products such as viscosity enhancing admixtures and superplasticisers. Esping (2007) reported that superplasticisers are used to improve the flowability of concrete. The effect of SPs on the constituents of cement paste is complex and has been the focus of much research. Superplasticisers react as soon as mixed with cement and water, and this influences the properties of SCC.

1.2 Research problem

The effects of ordinary Portland cements (OPC) produced in South Africa at different factories on SCC are not known. SCC requires a superplasticiser and the effects of different commercially available SPs on the self-compacting cement paste (SCCP) are also not currently understood.

1.3 Research question

What is the impact of PPC cement characteristics on the SCCP rheological behaviour?
What is the influence of chemical admixtures at their optimum dosages on these different cements in terms of yield stress, viscosity and thixotropy?

1.4 Objectives and outcomes

The aim of this research is to study the rheological behaviour of four cements manufactured by one company at four factories and investigate the impact of two SPs on their rheological behaviour.

For each type of cement, with and without SP, the objectives were as follows:

- to determine the evolution of yield stress over time;
- to determine the evolution of viscosity over time;
- to evaluate the rebuilding rate; and
- to determine the effect of cement properties on cement paste rheology.

The expected outcomes were as follows:

- the optimisation of SPs that involve the evaluation of the sensitivity of each cement in the presence of SP, in order to design an SCCP mix for a great SCC production;
- the change in viscosity over time of each cement at different constant shear rates;
- the measurement of hysteresis loops of each cement paste at a saturated dosage of SP for estimating their thixotropy;
- the evaluation of amplitude sweep and time sweep of each cement, with and without SP;
- the development of a new approach to evaluate the key rheological parameters of SCCP (yield stress and viscosity); and
- the establishment of a general kinetic equation of the self-acceleration type to follow the effect of hydration on the rigidification process of cement paste.

1.5 Significance

Since the implementation of SCC in the construction industry in the early 90s in Japan, most researchers have shown interest in attempting to more fully understand the rheological behaviour of this material when subjected to different stress conditions. Researchers have made a concerted effort, investing into this need in terms of investigations and the number of published papers. However, despite the available literature demonstrating the advantages that SCC offers, the acceptance of this new technology by the local construction industry is still quite minimal. This is due to the lack of SCC specifications and limitations in understanding of its rheological behaviour when using local materials (Geel *et al*., 2007). This present work contributes to the current knowledge about SCC in providing relevant information concerning the interaction of different local materials when used in the SCC mix, and their effects on the rheology of this material.

1.6 Delineation

This research only involved four types of cement produced by one company, and two types of commercial superplasticiser manufactured in South Africa. The effect of viscosity modifying admixture (VMA) was not considered in this work. Durability testing was also not included.

1.7 Assumptions

Few assumptions were made concerning the material used and the techniques applied in this research. The cement paste was assumed to be a colloidal material and all the theory developed for this type of material was applied to cement paste, such as consideration of the presence of internal forces and their interaction due to physical and chemical properties of the material. Since rheological measurements are influenced by many factors, it was assumed that the time of storage of the material had an insignificant effect on the measurement of rheological parameters, as the storage was quite short-term.

1.8 Methodology

The achievement of these research objectives required an experimental and comparative research design being approached simultaneously. The experimental work consisted of evaluating rheological parameters of cement pastes in the presence and absence of SPs, using three different techniques in two rheometric modes. The rheological parameters for each cement in both conditions of SP were compared to assess the effect of cement characteristics and the impact of SP on the flow properties of SCC. The experiments were conducted in the rheology laboratory of the Cape Peninsula University of Technology at the Flow Process and Rheology Centre (FPRC) using the MCR51 rheometer.

1.9 Organization of research

This research entails a full understanding of the effect and impact of cement characteristics and a new generation of SPs on cement paste rheology. A large number of experimental tests have been conducted in order to discover rational solutions to the problem stated. This current research is subdivided into six main chapters including the *Introduction (Chapter 1).*

Literature review (Chapter 2): The relevant theory describing cement paste hydration and its influence on the flow properties of SCCP is reviewed. The interaction between cement paste chemistry, mineralogy and superplasticers is also discussed. Rheological measurement techniques as used by various researchers are presented and discussed.

Research methodology (Chapter 3): The rheological measurement procedure from sample preparation to analysis of data is presented. The different modes of cement paste yield stress and viscosity measurements are explained in detail. A rheological approach is developed and introduced to follow the evolution of cement paste microstructure by monitoring the change of yield stress values over time.

Results (Chapter 4): After a thorough description of expected data and characteristics of material used, results regarding the flow properties, elastic properties and thixotropy of cement pastes are presented in separate sections. The flow properties comprised the values of yield stress and viscosity from both conventional flow curves and construction of flow curves. The elastic properties unveiled the yield stress values of cements with and without SP as determined in oscillatory mode in the linear viscoelastic domain. The storage and loss moduli of each cement under similar conditions are also considered. The thixotropy displayed the time dependency of each cement in both condition of SPs.

Discussion of results (Chapter 5): The rheological parameters as determined by each approach are discussed. A comparison between their estimated yield stress values is established. The effect of SP is investigated by comparing the rheological parameters of cement pastes without SP and those of cements with SP. A general kinetic equation of the self-acceleration type is suggested to quantitatively describe the rigidification process of cement paste. An attempt to link the characteristics of cement pastes to their rheological behaviours is made.

Conclusion (Chapter 6): A general conclusion related to the observation of the rheological properties of each cement in the presence and absence of SP is drawn. Relevant recommendations are suggested for further research and the contributions of this study in the field of interest are presented.

Chapter 2 Literature review and theory

SCC is a complex material that remains under investigation. The following section explores the relevant theory based on actual publications and investigations pertaining to the material under scrutiny. The principles of rheology applied to suspension materials are reviewed in details. The characterisation of materials, based on their rheological parameters as determined by constitutive equations are also discussed. In addition, the properties of SCCP are defined and their dependence on the microstructure of the paste is demonstrated. The effects of cement chemistry and cement-SP interaction on the rheological properties of cement paste during the early hydration are shown. Finally, the measurements of cement paste rheological parameters and the challenges encountered when using the current techniques are explained.

2.1 Introduction

This chapter contains two main parts. The first highlights the basics of rheology in general while the second part focusses on the application of rheology principles on self-compacting cement paste (SCCP). Based on this, the main factors that dictate the change in rheology of SCCP are discussed in depth.

2.2 Fundamental principles of rheology

2.2.1 Definition

There are several definitions of *rheology* available in the literature. Barnes *et al.* (1989) define *rheology* as the science of deformation and flow of matter. Banfill (2003) expands upon the definition by explaining the meaning of flow in the previous definition. Flow, he explains, infers a relationship between force, deformation and time. Rheology can therefore be used as a tool to characterise different sorts of materials comprised of ideal liquid through to ideal solid.

2.2.2 Rheological properties

In daily life, the observation of some material behaviour, when subjected to a certain amount of forces, has raised questions such as the following:

- Being in an identical container, why does water flow so much faster than toothpaste once overturned?
- Why, when increasing the stirring power on yogurt, does it becomes so much easier to stir over time, whilst when subjected to the same stirring power conditions, it is very difficult to turn oobleck (mix of water and cornstarch) over the same time of observation?

- Why doesn't paint run completely over when applied onto a vertical wall, whether glassy, masonry, or a steel plate wall?

These few questions demonstrate the complexity of some materials. So a theory had to be established to characterise their flow behaviour over time. There are actually two approaches that can be considered, as reported by Esping (2007): 1) the characterisation of the material can be done either by relaxation time, that is, the time required to reduce the stress in material by flow (Ferguson & Kemblowski, 1991); or 2) by defining the parameters that describe its flow behaviour. The latter approach was used during the course of this research in order to better understand the behaviour of cement paste under varying conditions.

It is important to understand the principles of rheology in order to know how and to what extent they can be applied to the material under investigation. The interpretation of rheological data also requires knowledge of these principles. First, materials vary from being an ideal liquid to ideal solid. An *ideal liquid* is defined as material that is not able to store energy due to the deformation undergone. This type of fluid can flow and the energy gained is dissipated as heat, causing a rise in temperature during the flow process. On the other hand, *ideal solids*, or elastic materials, are those which are able to store energy due to the imposed deformation and are able to fully recover their initial state once the imposed stress is released. Rheological characterisation of these materials under some circumstances of flow is quite easy and can be described by simple relationships (Tattersall & Banfill, 1983).

In practice, however, it is very difficult to find materials that behave as simply as explained above. Most industrial materials behave differently, exhibiting much more complex behaviour.

When considering the application of rheological principles and techniques to certain material of industrial interest, it is useful to know that most of these materials are a mixture of ideal liquids and ideal solids. These materials are partly liquid, or *viscous*, and partly solid, or *elastic*. Considering this, *viscoelastic materials* are defined as materials that are able to store some of the deformation energy while some is being lost by flow. The release of stress on these materials does not give them a chance to fully recover their initial state (Whorlow, 1992; Barnes *et al.,* 1989; Ferguson & Kemblowski, 1991).

2.2.3 Influencing factors

Most of the time, the deformation and flow behaviour of a material are affected by the following:

- *The inner structure of the material:* material with small particles that are close enough to each other will flow differently from ones with big particles that are distant from each other.

It is therefore easier to walk over a fine layer of sand than a layer of sand with large grains on the beach.

- *External forces:* material will flow and deform with respect to the applied force. The material can be pulled, compressed or wrapped around respectively when subjected to tension, compression, and moment or torsion force.
- *Environmental conditions:* the ambient temperature is the most significant environmental factor that can affect the flow behaviour of material.
- *Deborah number:* this parameter helps in achieving the scaling of time in rheology and gives an indication of whether solid-like or liquid-like behaviour is likely for a specific material (Banfill, 2003)**.** It defines the ratio between the characteristic of the deformation process being observed and the characteristic time of the material under investigation as per Equation 2.1:

$$De = \frac{t}{T} \tag{2.1}$$

Materials with high Deborah numbers exhibit solid-like behaviour and those with low Deborah numbers are liquid-like in behaviour, since it is accepted that *t* is infinite for ideal solids and zero for ideal liquids (Barnes *et al*., 1989).

2.2.4 Type of fluid

Considering the flow behaviour of materials, viscous materials are affected differently which allows for classifying them into two types (Hackley & Ferraris, 2001):

- ***Newtonian fluids***:
  This constitutes the ideal viscous liquid. Under a constant temperature, the viscosity of these materials does not change no matter how they deform. In other words, their viscosity is constant and independent of the shear rate. All gases and a certain number of common liquids including ethanol, water, most oils and some liquids with low molecular weight are Newtonian fluids.
- ***Non-Newtonian fluids***:
  Most of the viscoelastic liquids fall under this category of fluids. Their viscosity changes in a complex way over time. These materials do not obey the Newtonian relationship between shear stress and shear rate. Suspensions of fine particles are usually non-Newtonian.

Rheology is generally devoted to the study of these types of fluids in order to define and predict their behaviour.

2.2.5 Characteristics and type of flow

Considering a liquid in laminar flow (constituting infinite parallel layers of the liquid flow), as shown in Figure 2.1, a Newtonian liquid will exhibit different behaviour than a non-Newtonian liquid, depending on the flow characteristic and on the shear stress history exerted on the material over a certain period of time.

Flow characteristic

According to Tattersall and Banfill (1983), *viscosity*, referred to as the force that resists the flow of the material, is a very important parameter that defines the material. To define the viscosity of the material, a viscoelastic liquid is placed between two parallel plates distanced from each other of (y) distance. This height corresponds to the thickness of the liquid.

An applied force (F) on the upper plate of the surface area (A) while the underneath one stands still will cause a certain shear stress to the liquid as its parallel layers start moving. The *shear stress* applied on the liquid can be defined as Equation 2.2:

$$\tau = \frac{F}{A} \tag{2.2}$$

The shear rate determines the velocity gradient or the speed at which the different layers of the liquid are being sheared, defined as Equation 2.3:

$$\dot{\gamma} = \frac{v}{Y} \tag{2.3}$$

Sir Isaac Newton was the first to establish the proportionality between the shear stress and the shear rate when he observed the flow properties of an ideal liquid. This constant of proportionality noted by η was therefore defined as the viscosity of the material and represents geometrically the slope of the shear stress – shear rate line as in Equation 2.4:

$$\tau = \eta.\dot{\gamma} \tag{2.4}$$

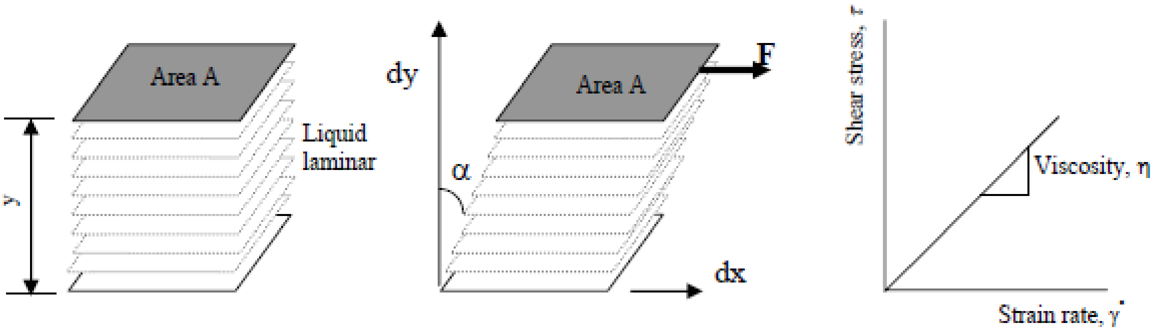


Figure 2.1: Newtonian’s law for viscous fluid (Banfill, 2006; Sheinn, 2007)

In addition, the flow of fluids does not only depend on their viscosity, as there are certain non-Newtonian fluids that will not flow unless a shear stress is applied. The initiation of such flow requires that a critical value known as the *yield stress* be exceeded.

Type of flow

As discussed above, the features of flow of a material are affected by the applied shear history and the corresponding viscosity. Several types of flow can therefore be classified based on the two properties of flow: yield stress and viscosity. This classification (Hackley & Ferraris, 2001) covers the most frequently encountered flow types divided in terms of Newtonian and General Non-Newtonian fluids.

- *Newtonian flow*

  This type of flow has to do with Newtonian fluids. These fluids are those whose shear stress is proportional to shear rate. Consequently, a Newtonian flow is characterised by a constant viscosity at a constant temperature, regardless of shear rate variation.

- *General Non-Newtonian flow*

  These fluids can flow once any amount of shear stress is applied and their viscosity can increase or decrease with time as the shear rate increases. In the first case, the flow is referred to as *shear thickening* or *dilatants*, and the second one as *pseudoplastic*. Certain non-Newtonian fluids will only flow when the yield stress has been overcome. These fluids are referred to as *viscoplastic* non-Newtonian and can exhibit different flow behaviour depending on the evolution of their viscosity within certain range of shear rate.

Where the viscosity remains constant during the flow, when the shear rate is increased, the flow will be referred as to *Bingham plastic flow*. In the case where the viscosity decreases continuously with an increasing shear rate, the flow is referred as *yield pseudoplastic.* Figure 2.2 illustrates these different types of flows.

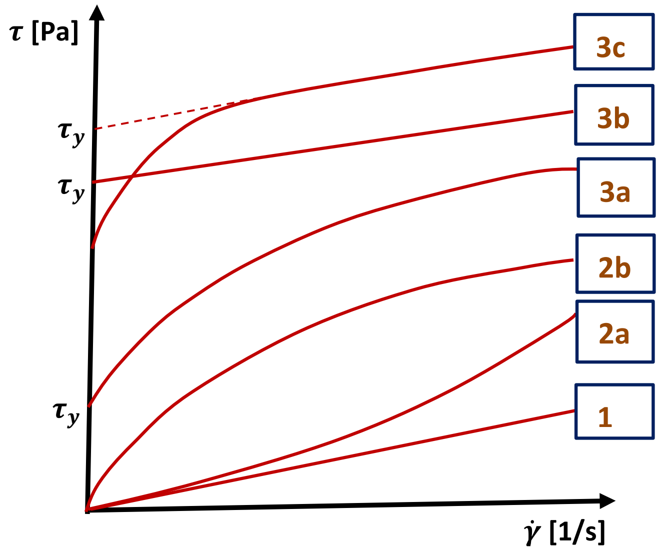


Figure 2.2: Illustration of flow properties: (1) Newtonian flow; (2a) general non-Newtonian with shear thickening; (2b) general non-Newtonian with shear thinning; (3a) viscosity non-Newtonian with shear thinning; (3b) viscosity non-Newtonian Bingham plastic; and (3c) viscosity non-Newtonian Bingham plastic non-ideal (Chhabra & Richardson, 1999)

2.2.6 Viscosity of suspension

For many years, the biggest need of engineers was to fully understand the behaviour of a given fluid in order to predict its flow properties. The first attempt by the pioneers of rheology was to characterise the fluid flow behaviour by defining its viscosity, since the flow properties of material depends mostly on this rheological parameter.

For dilute suspension fluid, Equation 2.4 can be used since the force of attraction between particles is very weak. However, for suspension materials, the viscosity is more affected by the volume fraction of solid particles and the extent to which the particles are flocculated (Eirich, 1956). Einstein described this relationship as follows in Equation 2.5:

$$\eta = \eta_c(1 + 2.5.\varphi) \tag{2.5}$$

where η_c is the viscosity of the medium. However, this equation was found to be ineffective when applied to fluids with high concentrations of particles, such as cement paste. As a consequence, the equation developed to suit these kinds of material was that which was proposed by Krieger-Dougherty as per Equation 2.5 (Krieger & Dougherty, 1959; Justnes & Vikan, 2005). The novelty of this equation is that the maximum packing fraction and shape of solids in the suspension were taken into account as follows:

$$\frac{\eta}{\eta_c} = (1 - \frac{\varphi}{\varphi_m})^{-x\varphi_m} \tag{2.6}$$

where φ_m and x are parameters accounting, respectively, for maximum packing fraction and shape of particles.

For complex material that involve a large number of parameters to be taken into account, such as cement paste, the mathematical expression of viscosity becomes difficult. The only solution that researchers have is to express the effect of water cement ratio on paste viscosity by establishing a certain number of mathematical models defining the shear stress with respect to shear rate.

2.2.7 Yield stress

The *yield stress* as per Beaupré *et al*. (2004) is the amount of shear required to initiate the flow of the fluid. In other words, yield stress is the amount of shear to be overcome by the fluid in order for the flow to start.

Yield stress can be explained by the presence of different forces – such as capillary, flocculation, colloidal, van der Waals, and electrostatic – that affect such material and whose interactions cause the repulsion or attraction effect between particles.

Flocculation and colloidal forces are the most predominant, and the resulting link between particles due to their interaction is weak to a point where a small amount of shear applied to the material is enough to break the link in question so the flow can start. The required shear stress to break this link between particles is referred to as *yield stress*.

2.2.8 Rheological models

In section 2.2.6, the difficulty to define the viscosity of suspension material was pointed out. The description of flow behaviour of most non-Newtonian materials is therefore done by means of mathematical models. These models are classified as per Chhabra and Richardson (1999) according to the number of parameters present. There are models with both two or three parameters.

- ***Rheological model with two parameters***

These models predict the flow behaviour involving only two parameters as noticed in the equations below.

Power law model

$$\tau = \kappa.\dot{\gamma}^{n} \tag{2.7}$$

Bingham model

$$\tau = \tau_y + \eta_{p.}\dot{\gamma} \tag{2.8}$$

Casson model

$$\sqrt{\tau} = \sqrt{\tau_y} + \sqrt{\eta_{p.}\dot{\gamma}} \tag{2.9}$$

- ***Rheological model with three parameters***

Herschel Bulkley model

$$\tau = \tau_y + k.\dot{\gamma}^{n} \tag{2.10}$$

Sisko model

$$\tau = \eta_y.\dot{\gamma} + k.\dot{\gamma}^{n} \tag{2.11}$$

Robertson stiff model

$$\tau = A(\dot{\gamma} + B)^{n} \tag{2.12}$$

In these models, κ is the consistency, n is the power law index, τ_y is the yield stress, η_p is the plastic viscosity, η_y is the viscosity at infinite shear rate, and A and B are constants.

2.2.9 Commentary on rheological models

From all these model parameters, it can be seen that the Herschel Bulkley model becomes the Bingham when *n* the power law index is equal to one. The consistency (k) corresponds then to the plastic viscosity. Robertson Stiff will describe very well the Newtonian fluid when *n* and *B* are respectively equal to one and zero. In that case, *A* defines the viscosity of the fluid. The same equation becomes Bingham model for *n* equal to one. In this case, the product *AB* defines the yield stress of the fluid, while *A* defines its viscosity.

It is easier to describe the shear thinning or thickening behaviour from a model that includes the power law index such as the Herschel Bulkley model. Justnes and Vikan (2005) suggested measuring the plastic viscosity at low shear rate (μ_{pl}) and at medium shear rate (μ_{pm}) in order to distinguish the two types of shear. They recommended to evaluate the ratio between these two types of viscosity $\frac{\mu_{pm}}{\mu_{pl}}$ so that if the ratio is less than one, shear thinning behaviour is exhibited; if more than one, shear thickening behaviour is exhibited; and if equal to one, Bingham plastic or Newtonian behaviour is exhibited. This is because both behaviour would produce a ratio of unity.

The research conducted by Sheinn (2007) makes clear the need for establishing these mathematical models. With the availability of these models, the yield stress is calculated by extrapolation, since it is very difficult to compute the shear stress at zero shear rates. He investigated the yield stress predicted by different models using two different test geometries – coaxial cylinder and parallel plates – and found that the Herschel Bulkley model estimated the highest yield stress values for both test geometries. The Bingham model, however, estimates lower yield stresses when using the parallel plates. It is important to mention that these levels of yield stress values as predicted by these models would strongly depend also wheter the material is shear-thining or shear-thickening.

Justnes and Vikan (2005) made a few comments on the comparative work conducted by some researchers and demonstrated the disagreement that still exists between scientists when it comes to the selection of which model better describes the behaviour of cementitious paste. However, Sheinn (2007) states that the Bingham model is the most popular constitutive relationship used to describe the flow properties of cementitious materials. This model takes into account the stress that must be overcome by the cement paste before it starts to flow. The yield stress indicates the destruction of internal static structures present in the flocculated suspension. The Bingham and Herschel Bulkley models are thus preferred over other models for the simple reason that their parameters can be measured independently and the flow of cement paste seems to be very well predicted by these constitutive equations.

2.2.10 Rheometer

Rheological models become more meaningful when the shear stress and shear rate data can be determined. This is made possible by the use of different physical instruments available in industry such as the rotational or oscillation rheometer used for this purpose: the former is more suitable for liquid-like material, and the latter for viscous to solid materials.

A rheometer uses the principle of two plates, as explained in section 2.2.5 and demonstrated in Figure 2.1. The outer cylinder corresponds to the fixed plate, the inner bob to the mobile plate. The rheometer uses the technique of either pre-setting the shear stress and the shear rate is recorded, or pre-setting the shear rate and the shear stress is collected.

In a rotational motion, the rotational speed and the torque or the force applied to the rotation must be considered, as this makes possible the control of the flow of the liquid as one can fix how fast the bob will rotate. The expected result will be the torque required by the liquid depending on its viscosity in order to cause the shearing. This set-up can be done the other way around as well. That is, one can fix the torque and measure the speed of the bob.

Shear stress can be derived from torque and shear rate from rotational speed. Software incorporated within the rheometer makes possible to compute these conversions easily.

From the above, two types of rheometers can be defined: CSR (control shear rate) and CSS (control shear stress). With a CSR rheometer, shear rate is pre-set and shear stress is recorded as the output of the measurements. Alternatively, with a CSS rheometer, the pre-set parameter is shear stress, and shear rate is measured.

2.3 Self-compacting cement paste rheology

The importance of measuring rheological behaviour of self-compacting concrete (SCC) on self-compacting cement paste (SCCP) scale is reviewed in the following section.

Concrete as a complex material can be reduced to different simple components, as illustrated in Figure 2.3. On a larger scale, aggregate can be considered as a suspended solid, and mortar the suspending medium, whilst on a mortar scale, fine aggregates constitute the solid phase and cement paste the liquid phase. At paste scale, the powder (cement or other fillers) is considered solid material, while water constitutes the liquid phase (Sheinn, 2007).

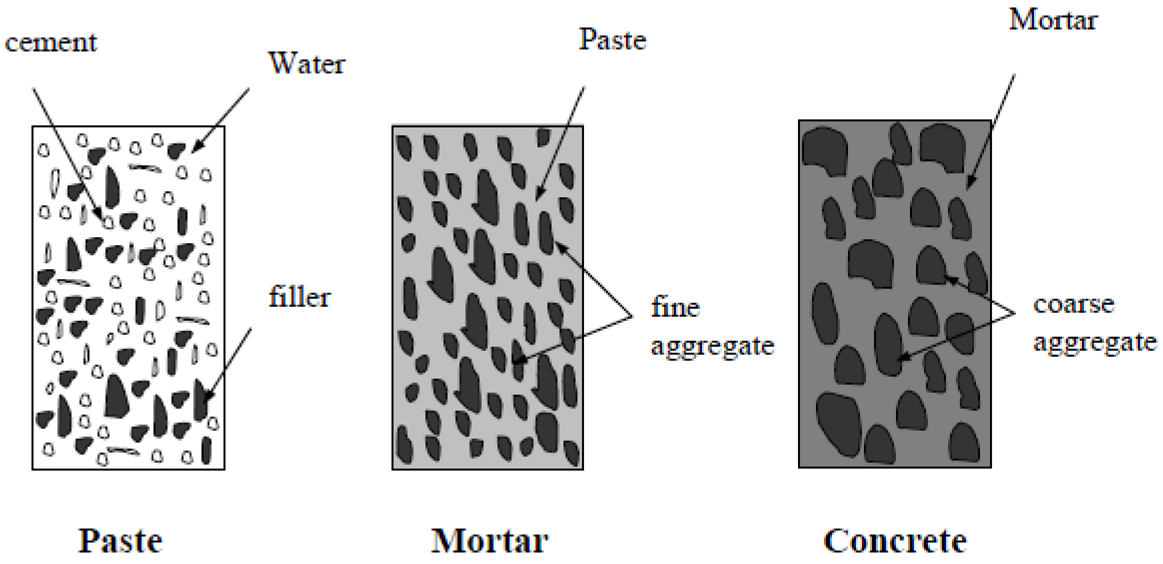


Figure 2.3: Suspension theory for different components of concrete (Sheinn, 2007)

2.3.1 Definition of self-compacting concrete

SCC is concrete that is able to flow under its own weight and completely fill the formwork, even in the presence of dense reinforcement, without the need for any vibration, yet whilst maintaining homogeneity (Sheinn, 2007). It has a high tendency to deform while performing a great resistance to segregation (Schwartzentruber *et al.,* 2006).

This implies conditions regarding the properties of concrete that need to be met for a concrete to qualify as SCC. The three most important properties of SCC are flow ability, passing ability and the resistance to segregation.

According to Schwartzentruber *et al.* (2006), the prevention of segregation in SCC is achieved by improvement of the cement paste rheology. This must be fluid enough to allow for the flowability of the fresh concrete, yet viscous enough to ensure the support of coarse aggregates. Both yield stress (minimum amount of stress required to initiate flow) and viscosity (resistance to flow) of cement paste enable the concrete to avoid the initial segregation and minimise the effects of this phenomenon. Since cement paste is very sensitive to admixtures used to produce SCC, it is important and useful to evaluate the rheological behaviour of cement paste to obtain a macroscopic picture of SCC rheology.

2.3.2 Self-compacting cement paste properties

Studies conducted by Hildago *et al.* (2008) confirmed that the purpose of improving rheological properties of cement paste is to produce a stable concrete.

Libre *et al.* (2010) state that concrete with good workability is achieved by increasing its fluidity. The workability itself is governed by the water content, and chemical and mineral admixtures. However, a high fluidity is not always recommended, for this can be a source of cementitious material instability which can be displayed in various forms such as bleeding, coarse aggregate settlement and blocking. Due to the migration of water within the fresh concrete, internal bleeding has to be distinguished from surface bleeding.

A proper workability is not only achieved by increasing the fluidity of the concrete, a good workability also requires that the concrete has a great stability. SCC is therefore defined as a concrete with high fluidity and adequate stability (Libre *et al*., 2010).

Adequate fluidity is obtained by optimum water content whilst the stability is achieved by the incorporation of mineral or chemical admixtures such as viscosity modifying agents (VMA) and superplasticisers (SP). The increase of yield stress and viscosity can assist in decreasing the risk of segregation, as stated by Schwartzentruber *et al*. (2006). These researchers agreed that there might be an acceptable range of these two rheological parameters whereby segregation is minimised, while allowing the material to flow under its own weight.

Designing an optimum mix that meets these criteria certainly isn’t easy, because the improvement of one property is done at the cost of the other. For instance, increasing the w/c or superplasticiser content is very effective in improving the fluidity, while decreasing stability and VMA or fine-graded filler used to improve the stability of SCC tends to decrease its fluidity. So, in order to obtain a good SCC mix, both stability and fluidity need to be optimised.

Flowability

SCC is required to flow under its own weight and fill all spaces within the form work. The achievement of this property needs a balanced w/c ratio. The greater this ratio is, the higher the flowability will be. It is agreed that the strength of concrete is inversely proportional to the w/c ratio. Equation 2.13 describes the relationship between the strength of concrete and the w/c ratio:

$$f_c = \frac{k_1}{k_2^{\,w/c}} \tag{2.13}$$

where f_c is the compressive strength, and k_1 and k_2 are empirical constants. However, the w/c ratio isn’t the only factor that affects the flowability of concrete; the aggregate-cement ratio does as well, as the inter-particle forces in the cement paste are affected by the friction between aggregate particles. A higher aggregate-cement ratio espicially in “dry” concrete mixtures results in a high amount of aggregate interlocking, causing greater inter-particle friction and yielding a concrete with a poor flowability (Sheinn, 2007).

Passing ability

SCC must be able to flow and pass through the spaces between the reinforcement bars and formwork without creating any kind of blockage. Since the flow of the concrete through openings will require the deviation of aggregate from their flow path, there might be collisions among aggregates just at the entrance of the opening, resulting in the formation of an arch that prevents the flow of the concrete. Avoiding concrete with poor passing ability requires minimising the collision between coarse aggregate particles. Allowing for a large quantity of cement paste that helps to lubricate the aggregate in the SCC is one way to achieve this property (Sheinn, 2007).

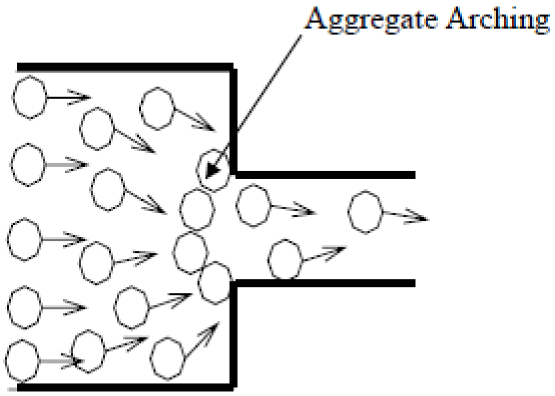


Figure 2.4: Formation of aggregate arching (Sheinn, 2007)

Resistance to segregation

Resistance to segregation is a phenomenon that has always been related to plastic viscosity (Diamantonis et al., 2010) and density of the cement paste for the simple reason that when in a suspension material, the density of suspended particles is higher than that of the suspension medium, so the solid particles will settle inside the liquid. It is more convenient, therefore, to increase the viscosity of the cement paste and its density (since the presence of free water in the mix reduces the viscosity) making the cement paste thick enough to prevent the occurrence of segregation. However, other researchers believe that the yield stress of cement paste is still the main parameter preventing segregation to occur as discussed in section 2.3.1.

2.3.3 Microstructure of cement paste and its time dependency

From the above, it is clear how relevant the viscosity and yield stress of the cement paste are for the effective performance of SCC. A low viscosity is required for flowability of SCC, but the cement paste has to be viscous enough to avoid segregation. Improving the properties of cement paste requires understanding the rheological properties such as viscosity, yield stress and thixotropy.

Cement paste, as a suspension and time-dependent material, is not spared from these rheological steps: rest, application and recovery. The knowledge of its behaviour at each step in terms of its viscosity and yield stress is imperative. In other words, knowing how fast the cement paste will liquefy and recover its viscosity is the key to mastering the rheological properties of this suspension material. *Thixotropy* as defined by Khayat *et al.* (2012) is a gradual loss of cement paste viscosity over time during flow process and restoration of its initial structural state once at rest. The time dependency behaviour of cement paste can only be estimated by measuring its thixotropic property (Wallevik, 2005).

In his research, Quanji (2010) shows the difficulty of defining the thixotropy of cementitious materials based on the basic physical principles of thixotropy. He therefore relates the thixotropy of cement paste to its microstructure knowing that the latter is affected by the hydration process. Hence, based on the microstructural point, the thixotropy properties of cement pastes come from the break of flocculation or connected particles.

Conversely, the physical principles of thixotropy properties of cementitious materials are as explained in the schematic representation in Figure 2.5.

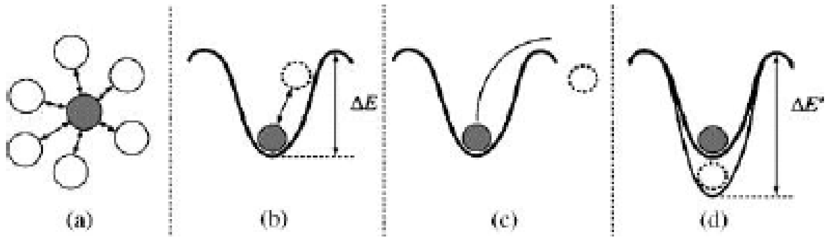


Figure 2.5: Schematic explanation of thixotropy of cementitious material (Quanji, 2010)

Figure 2.45 (a) indicates the balanced position for each cement particle due to a small potential energy ∆E. When there is an applied external energy exerted on the particle, the latter will not move from its position unless this applied energy is above a certain amount, as shown in Figure 2.45 (b) and (c), and only then will the flow be initiated. After the particle has left the energy well, the later returns to its initial depth as shown in Figure 2.5 (d).

The energy that provokes this movement of particles is not only due to the changes that take place during cement paste hydration, but also to the interaction between particles.

Another way to explain the thixotropy of cement paste is demonstrated in Figure 2.6.

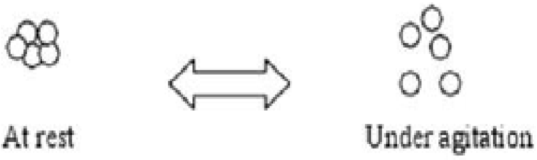


Figure 2.6: Thixotropy behaviour of cement paste (Quanji, 2010)

When there is no applied shear, cement paste particles coagulate. Then, as soon as external shearing is applied, particles are conditioned to separate from one another. The reversible behaviour of this process, coagulation-separation-coagulation, defines the essence of thixotropy of cement paste.

Tattersall and Banfill (1983) affirm that in cement paste there is an electrical field present in the suspensions due to the charge that each particle bears. The sign of the charge will depend on the nature and the adsorption of ions on the surface of a particle layer. However, the charges are distributed on particles in a way that conserves the electrical neutrality of the suspension, made possible by the presence of an electrical double layer comprised of the actual particle charge and counter-ions on each particle surface, as illustrated in Figure 2.7.

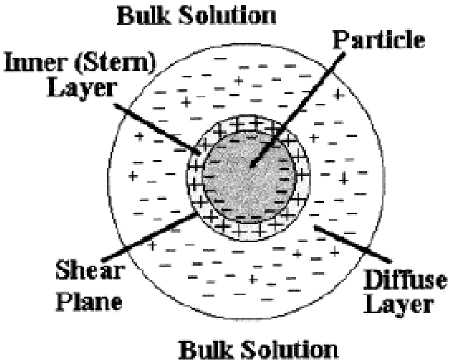


Figure 2.7: Electrical double layer on cement paste (Quanji, 2010)

When two particles approach one another in a suspension, their double layer will begin interfering due to the charges they are carrying. This situation changes the distribution of ions in the particles' double layers so that the free energy of the suspension increases up to an amount corresponding to what Vikan (2005) refers to as the maximum of the total or interaction energy, V_{max}, the particle has to overcome to coagulate. At this stage, where the free energy is equal to V_{max}, particles experience a repulsive force and repulse each other. However, the repulsive energy (V_R) decreases exponentially with the distance between the two particles. As the particles keep moving toward each other, the distance separating them decreases and the maximum interaction energy consequently decreases to the primary minimum of the total energy (V_T,). Attractive forces (V_A) become more pronounced between particles, so as they attract each other, coagulation occurs. This phenomenon is visually clarified in Figure 2.8.

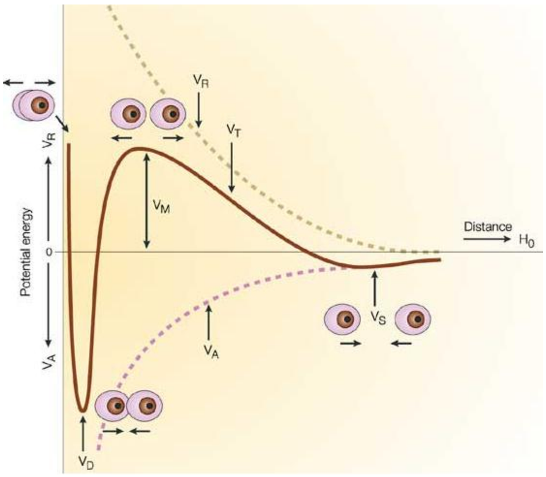


Figure 2.8: Total potential energy evolution between two distinct cement particles (Vikan, 2005)

Quanji (2010) recognised that when considering the effect of shearing micro-structurally, particles will put themselves into lines parallel to the shear direction, and once the deflocculation and dispersion of particles take place, the viscosity of the material will decrease to a certain steady value. Afterwards, when the paste is at rest, the re-connection and re-coagulation of particles will take place, inducing an increase in viscosity as before. Thixotropy does affect the yield stress as well, in the sense that the re-building of the cement paste micro-structure takes some time. Thus, the yield stress of cement paste will increase as the resting time after shearing is prolonged.

2.3.4 Cement characteristic and paste rheology

Cement chemistry

Portland cement consists mainly of four raw materials: lime, silica, alumina and iron oxide (Nelson *et al.*, 1990). These materials come from different sources: lime comes from calcareous rock and alkali waste from some factories, whilst silica, alumina and iron oxide come from clays.

These four materials are combined in the form of powder and heated at temperatures of about 1500º C. At these temperatures, the materials undergo chemical reactions in a rotating kiln that yield the four main compounds that form cement:

1. Ca_3SiO_5 tricalcium silicate;
2. Ca_2SiO_4 dicalcium silicate;

3. $Ca_3Al_2O_6$ tricalcium aluminate; and
4. $Ca_4Al_2Fe_2O_{10}$ tetracalciumalumino ferrite.

These compounds come out of the kiln as clinker after cooling. A certain amount of gypsum is then pulverised and ground to obtain the finished Portland cement.

The industry abbreviates:
Al_2O_3 →[A]
CaO→ [C]
Fe_2O_3→ [F]
SiO_2→ [S]
Na_2O → [N]
SO_3→ [S^-]
H_2O →[H]

The four cement compounds are named as follows (Zhang *et al*. 2010; Hall, 2009**;** Kurtis, n.d.)**:**

1. Ca_3SiO_5: C_3S [Alite]
2. Ca_2SiO_4: C_2S [Bilite]
3. $Ca_3Al_2O_6$: C_3A [Aluminate]
4. $Ca_4Al_2Fe_2O_{10}$: C_4AF [Ferrite or Brownmillerite]

The $C\overline{S}$ is referred as to Anhydrite and is added to the mill during the clinker grounding process (Vikan, 2005). Figure 2.9 and 2.10 illustrate the entire manufacturing process of cement:

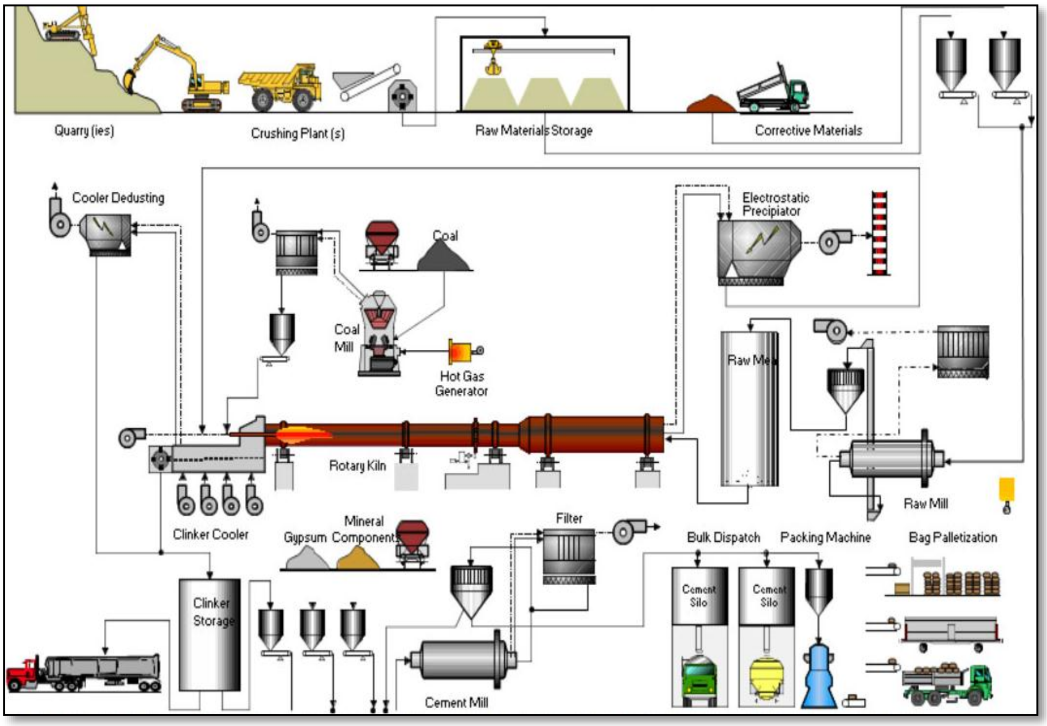


Figure 2.9: Process flow diagram of the cement manufacturing process at a local plant (www.engineeringintro.com)

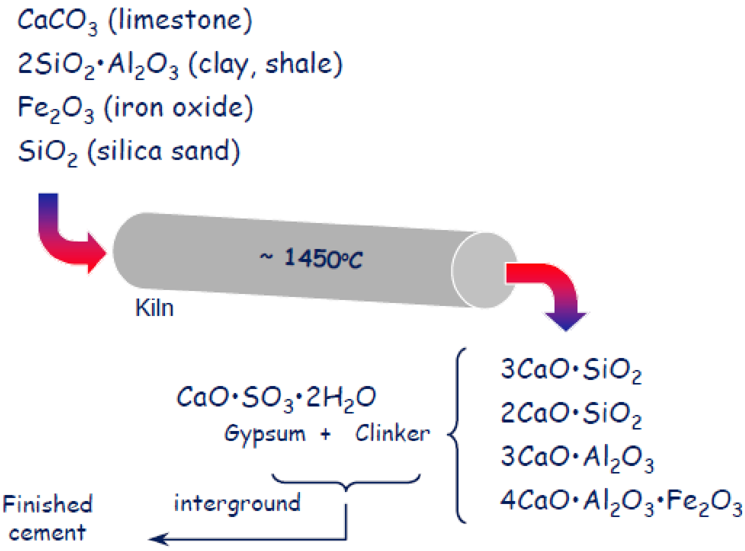


Figure 2.10: Cement compound formation after kiln process and grounding (Kurtis, n.d.)

These compounds form the clinker structure at different concentrations, as shown in Figure 2.11. Depending on the type of Portland cement, these compound concentrations may vary from one cement type to the other. However in general, Alite concentration will be in the range of [28 – 56%], Bilite [19 – 46%], Aluminate [4 – 14%] and Ferrite [2 – 12%] (Swan, n.d.).

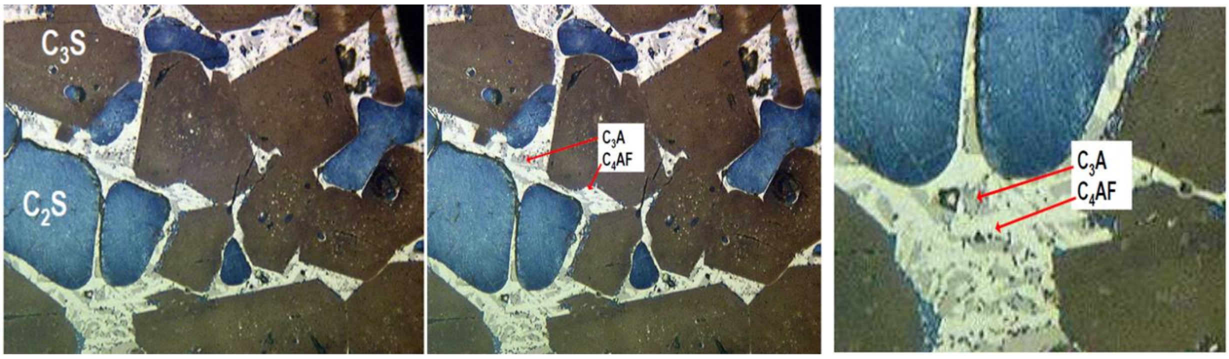


Figure 2.11: Cement clinker microstructure (Hall, 2009)

The concentration of these compounds in clinker is calculated through mass balances by Bogue calculations in the case where firstly, these four minerals are present, and secondly, the equilibrium was reached during the cooling of the clinker during production (Vikan, 2005).

$$C_3S = 4.07C - 7.6S - 6.71A - 1.43F \quad (2.14)$$

$$C_2S = -3.071C + 8.6S + 5.068A + 1.079F \quad (2.15)$$

$$C_3A = 2.65A - 1.692F \quad (2.16)$$

$$C_3AF = 3.043F \quad (2.17)$$

According to Moore (1982), Equations 2.14 – 2.17 indicate only the potential composition of the clinker, because it is not always obvious that reactions taking place during the kiln process will go to completion. Vikan (2005) reported that the results of these equations differ from the true phases by overestimating C_2S and underestimating C_3S. Ferrite is frequently underestimated while aluminate overestimated, for example. Therefore, he suggested another method that defines the four clinker phases in terms of three parameters:

Silica ratio (SR): this takes into consideration the burnability of raw mix and gives an indication of how much energy is put into the system.

Alumina-iron ratio (AR): this helps with controlling the potential C_3A/C_4AF ratio in cement that gives an idea about the sulfate resistance, heat generation and admixture compatibility issues.

Lime factor (LF) and lime saturation factor (LSF): these control the potential C_3S/C_2S ratio in cement.

$$SR = \frac{S_iO_2}{Al_2O_3} + Fe_2O_3 \tag{2.18}$$

$$AR = \frac{Al_2O_3}{Fe_2O_3} \tag{2.19}$$

$$LF = C - \frac{(1.65A + 0.315F)}{S} \tag{2.20}$$

For MgO < 2%

$$LSR = \frac{100(CaO + 0.75Mg)}{(2.85S_iO_2)} + 1.18Al_2O_3 + 0.65Fe_2O_3 \tag{2.21}$$

For MgO > 2%

$$LSR = \frac{100(CaO + 1.5Mg)}{(2.85S_iO_2)} + 1.18Al_2O_3 + 0.65Fe_2O_3 \tag{2.22}$$

The Rietveld analyses of X-ray diffractograms or optical microscopy are widely used with more accuracy for this purpose as well. However, the latter method has a few disadvantages, primarily the time required to carry out the experiments and the difficulties that occur during the Aluminate phase determination due to their micro-crystallinity.

Other indications on cement specification data sheets are vital to be highlighted, such as alkalis that are found as mineral aphataline in solid solution in the main minerals. Free lime is referred to as the free CaO content that comes from the insufficient decomposition or burning of C_3S when the cooling is low.

Cement characteristic

The rheological characterisation of cement paste takes into consideration many intrinsic variables of cement. Vikan *et al.* (2007)**,** studying the effect of cement characteristics on flow resistance, found that cement cannot be treated as a uni-variable material. They considered four cements with similar clinker, different only in fineness, and observed that it was possible to characterise the four cements. That is, the flow resistance in this case was an exponential function of the cement Blaine.

However, there was no correlation expressing the flow resistance when cements were different in clinker *and* Blaine. They concluded by suggesting that rheological properties depend on more than one variable of cement, such as fineness and chemical composition (C_3A, C_2S, C_3S, alkali) contents. That is, rheological properties were found to be related to both chemical and physical properties of cement.

Aiqin *et al.* (1997) concentrated most of their research on attempting to assess the impact of particle size distribution (PSD) of cement on paste properties. They found that the PSD influences the rate of hydration and the packing density. These have a major impact on the porosity within the paste that governs the cement paste mechanical properties. They proved that the narrower the PSD is, the faster the rate of hydration will be. Cement with a wide PSD will have a higher packing density while cement with homogenous PSD will have a higher degree of hydration. The balance is found to be where the diameter of the small to the large particle is equal to 0.3.

Celik (2009)**,** examining the effect of PSD on cement properties emphasising the uniformity factor (n) that determines if either the distribution of particle is narrow or wide, reported that water demand, hydration and setting all depend on the PSD. The properties start being affected when the size of particles are in the range of 0 – 30 µm, and particles play the role of filling effect when they are above 60 µm. Celik suggested that the PSD should be continuous and steep, with fineness between 2500 and 3000 cm^2/g.

Aiqin *et al.* (1997) found that both the fineness and specific surface area (SSA) have an impact on the compressive strength of the cement paste: cement with narrow PSD will have a higher strength than cement with a wide PSD, for example. Their research explains the reason why the fineness of cement affects the compressive strength only at early age (between one to three days). The fact is that the hydration at an early age depends mostly on the particle surface upon which water acts.

Focusing on the effects of chemical composition of the cement on the cement paste properties, Aiqin *et al.* observed that cements with higher C_3S content were gaining strength more quickly than those with higher contents of C_2S. They noticed that C_3A was contributing to compressive strength only at the very early age stage. C_4AF though was not influencing the compressive strength at early or later age. Similarly, Lapasin *et al.* (1983) highlighted the contribution of each single compound on the rheological properties of cement paste. Since C_3S hydrates and hardens rapidly, it is responsible for initial set and early strength. C_2S has the ability to hydrate and will harden at a slow rate, contributing to strength only after seven days. C_4AF reduces clinker temperature and hardens rapidly without much contribution to strength. This compound is responsible for the grey colour of the cement paste. As an illustration, Figure 2.12 shows the contribution of each cement compound on the compressive strength.

While previous research focused only on the influence of the main cement mineralogy compounds on the paste rheological behaviour, Pedrajas *et al.* (2014) revealed a critical point concerning the impact of other chemical compositions on paste rheological properties. They investigated two different cements with different mineralogy: Na_2O and K_2O content. The cement with higher contents of C_3S and C_2S was expected to have more strength than the other, but results showed a different scenario. They stated that the difference was in the Na_2O and K_2O (alkali) content. Cement with higher alkali content had a lower shear stress regardless of C_3A content, the reason being that the higher concentration of alkali was raising the pH of the paste in the liquid phase as NaOH and KOH could not precipitate during hydration.

Hanehara and Yamada (1999) investigated four different types of cement produced from different plants and found that their rheological properties were only slightly different, but when superplasticisers were added, the difference was significant. They noticed that each type of SP affected each type of cement in very different ways, depending on the chemistry of the cement.

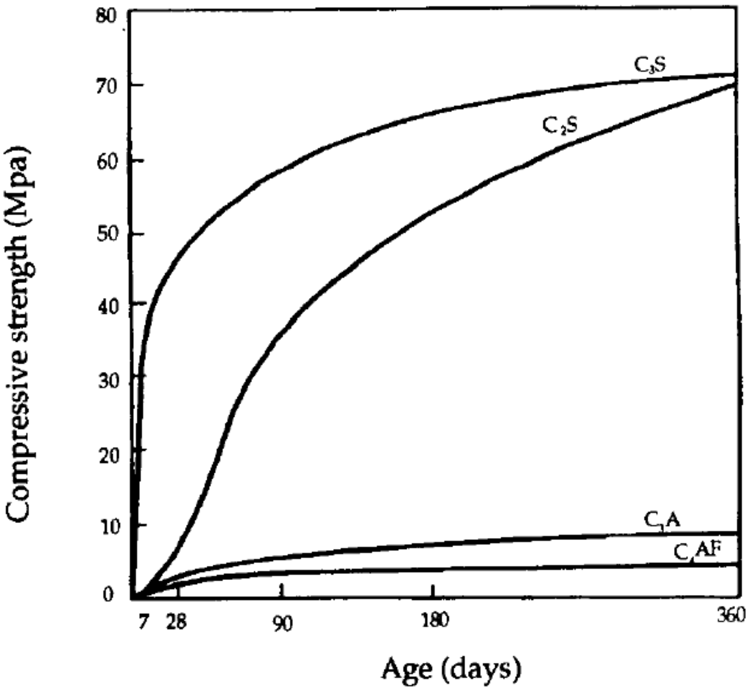


Figure 2.12: Contribution of cement compound on compressive strength of cement (Zhan & Napier-Munn, 1995)

Golaszewski (2008) investigated the influence of cement properties on cement mortar rheology and suggested that this can assist in developing a clear understanding of the rheological behaviour of concrete. In his findings, he pointed out that the most important compounds of cement that influence the rheological behaviour of mortar at early age is the C_3A content, followed by the cement specific surface area and the Na_2O_{eq} content. He confirmed that the SO_3 content has no great influence on the rheological behaviour of either paste or superplasticised paste.

However, Golaszewski's experience demonstrated that an increase of C_3A content leads to an increase of the yield stress, while the plastic viscosity decreases. The cement with low C_3A content experiences a small reduction of yield stress when the specific surface is increased, and the cement with higher C_3A content experienced increase of yield stress under the same conditions. However, the plastic viscosity decreases with the increase of the cement specific surface.

Vikan *et al.* (2007) established the correlation as described by the equation below between the cement characteristic and the flow resistance, defined as the area below the flow curve for a certain range of shear rates. The flow resistance is expressed as an exponential or linear function of the cement characteristics depending on the superplasticiser and dosage used.

Flow resistance = Blaine. [d.cC_3A+ (1-d).C_3S] or flow resistance = a.exp (b.Blaine. [d.cC_3A+ (1-d).C_3S]) where d is the relative reactivity in cement paste; c stand for cubic; and a and b are factors of linearisation.

2.3.5 Influence of hydration kinetic and yield stress development on cement paste rheological behaviour

Hydration kinetics of cement

Contrary to common perception, the hydraulic Portland cement does not set or develop its compressive strength by drying out, but rather through hydration whereby chemical reactions take place between water and the cements compound. This gives Portland cement the ability to harden, whether in air or under water.

It is important to understand how the different cement compounds react with water. *Hydration* is referred to as the reaction that takes place immediately when water comes into contact with cement. This reaction goes through different phases that are dictated by each of the compounds. Bishnoi (2008) stated that these cement phases react and occur respectively at different times and at variant rates. Some researchers tend to overlook the hydration kinetic in the *dormant stage,* defined as the period between the time water is added to cement up until the initial setting (Tattersall & Banfill 1983). However, Vikan (2005) stated that the products of hydration are affected during this period. Roussel *et al.* (2012) demonstrated the influence of hydration kinetics during this period on the evolution of particle network within the paste as well.

- ***C_3A phase***

This is the most sensitive mineral to water at the very early stage of hydration. The product of this phase, as well as its rate, will be different from the case where impurities such as calcium sulfate are present or absent in the cement.

In fact, in the presence of calcium sulfate, C_3A hydration will yield ettringite (Aft), needle crystal-like materials referred to as *trisulphate*. Figure 2.13 shows how these materials precipitate on the C_3A surface. Due to their nature (they take up much water, contributing then to the stiffening of mixture) they hinder further hydration. The ability of ettringite to slow down the hydration process has been argued by many researchers who have tried to explain the phenomenon in other ways.

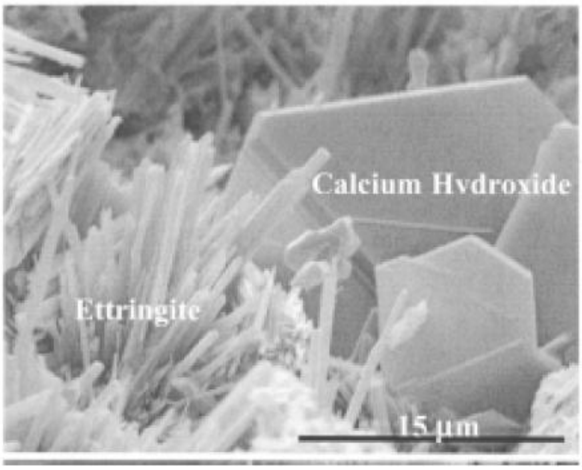


Figure 2.13: Precipitation of ettringite on C_3A within cement paste during Aluminate phase hydration

Regardless of these arguments, it is agreed that the presence of calcium sulfate hydrate (gypsum) in cement is very important as it helps the fresh cement to remain fluid for a few hours. In fact, if there is no gypsum in cement, C_3A hydrates very quickly, causing the cement to set in just a few minutes (flash setting) altering the workability of cement paste.

$$C_3A + 3C\overline{S}H_2 + 26H = C_6A\overline{S}3H_{32} \tag{2.23}$$

The formation of ettringite is characterised by a significant heat liberation with a rapid reaction at the beginning, slowing down significantly thereafter. The duration of this period varies and is proportional to the amount of calcium sulfate in the original cement.

In the absence of calcium sulfate, C_3A yields a gel-like material that develops at the C_3A surface. As the hydration continues, this product changes into hexagonal crystals, C_2AH_8 and C_4AH_{19}. These materials play for a hydration barrier, consequently slowing down the hydration process. These materials transform into C_3AH_6 later on, disrupting the diffusion barrier and the hydration proceeds normally at high speed.

$$2C_3A + 27H \rightarrow C_2AH_8 + C_4AH_{19} \rightarrow 2C_3AH_6 + 15H \tag{2.24}$$

Alternatively, impurities that introduce foreign ions into the crystal structure of C_3A have a major impact on both the morphology of this compound and the rate of hydration. Vikan (2005) mentioned that in the case where there were no impurities in the cement, C_3A hydration rate was evaluated at about 60% at ten minutes and in the reverse case, the rate of hydration was about 43 or 37% depending on the nature of impurities.

Hanehara and Yamada (1999) affirmed that this phase is more affected by the concentration of Ca^{2+}, OH^- and SO_4^{2+} that depends on the amount of alkali, gypsum content and free lime in cement. This statement concurs with the findings of Pedrajas *et al.* (2014) as discussed above, since it is clear how a high concentration of alkali can raise the pH of the solution in early hydration. They observed again that in high concentration of ions, a small amount of ettringites is produced, covering the unreacted C_3A/C_4AF as explained above, and slowing the rate of hydration. In low concentration of ions, large amounts of ettringites will be produced continuously, causing the stiffness of the cement paste.

- ***C_3S and C_2S phases***

C_3S and C_2S are the most important constituents of cement for they represent 80% of Portland cement and yield the same hydration products that influence the cement paste rheological behaviour. However, C_2S hydrates differently to C_3S in the sense that, at early age of hydration, this compound hydrates to a small extent and its hydration continues at a later stage.

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{2.25}$$

$$2C_3S + 4H \rightarrow C_3S_2H_3 + CH \tag{2.26}$$

According to Bishnoi and Scrivener (2009), the effect of C_3S hydration on cement paste can already be seen a few hours after mixing has taken place. Since it is difficult to follow the hydration of each cement compound individually, researchers use heat evolution to monitor the overall hydration of cement. The hydration process is subdivided into five stages, as illustrated in Figure 2.14, which are the result of the combined effect of more than one cement phase.

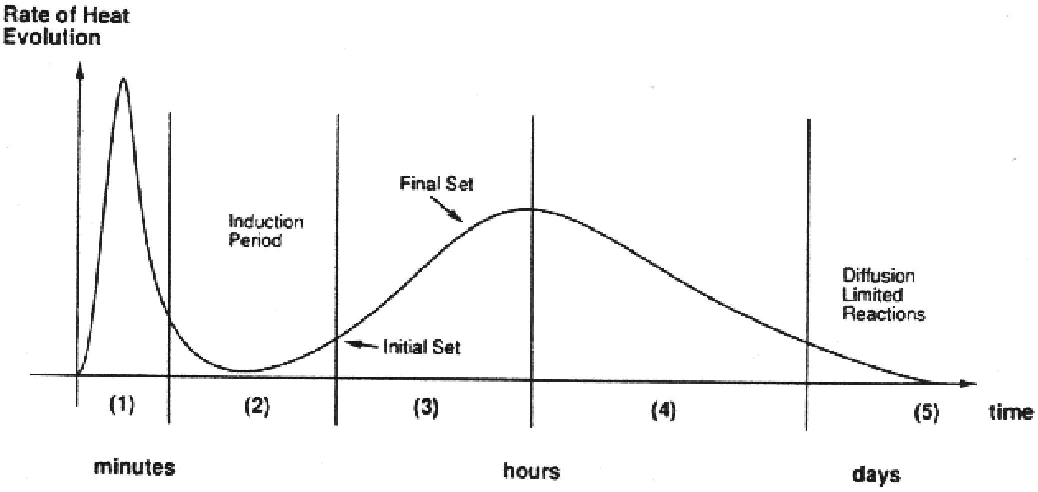


Figure 2.14: Evolution of heat during the cement hydration (Vikan, 2005)

The heat evolution during the hydration of alite follows the same trend as the general heat evolution of cement hydration. Some researchers divide its hydration process into four steps, and others into five. In fact, as soon as water comes into contact with cement, the dissolution of C3A happens, causing a large amount of heat to be released. This corresponds to the first peak of Figure 2.14. However, C3S may be dissolved as well at the same period of time and yield some hydration products.

This first step is referred to as the ***dissolution period***. This period corresponds to the first stage of heat evolution of cement. It has been proven that the dissolution of C_3S in this period depends closely on a few factors, including the particle size. After a few minutes, the dissolution becomes less intense and a significant decrease of heat can be observed. Due to the saturation of CSH formation, the dissolution slows down and the second step starts.

The second step is referred to as the ***induction period***. This corresponds to the second stage of the general heat evolution and is referred to as the dormant stage. However, the hydration continues at a low rate followed by a low heat evolution. This period can last about an hour.

The third step is referred to as the ***acceleration period.*** During this step, the hydration suddenly accelerates until it reaches a peak. The cause of this acceleration has never been fully understood and so remains under investigation, but some researchers agree that it is a result of a decomposition of a protective layer that was formed in the reaction at the initial stage.

The last step in Alite hydration is called the ***deceleration period*** and corresponds to the last stage of hydration. In this period, the reaction slows down quickly as a large amount of C_3S is being consumed. The decrease of the reaction is explained by some researchers as the fact that the rate of hydration is controlled by the diffusion of a thick layer growing over unhydrated cement particles as the hydrates are being deposited around them. For this stage to occur, the diffusion of the said layer and the availability of material are required.

Work conducted by Vikan (2005) showed that during hydration, the C_3A phase is the most active mineral during the initial couple of hours and that the Alite hydration starts only approximately two hours after the mixing. Similarly, Nelson *et al.* (1990) confirmed that Aluminate has a higher degree of reactivity at the beginning of hydration, influencing the rheological properties and the strength of cement paste.

Yield stress development

It has been stated by Rahman *et al.* (2014) that the hydration kinetics phases have a major influence on rheological properties of fresh cement paste. Silicate and Aluminate molecules are charged positively and have the capacity to attract the negative molecules of water. As the hydration progresses, the properties of cement evolve from viscous fluid to solid material. Swan, (n.d.) and Hildago *et al.* (2008) refer to this transformation of cement from fluid into a solid material as *setting*. The latter depends on the product of hydration phases. Figure 2.15 illustrates the dependence of cement setting on hydration development.

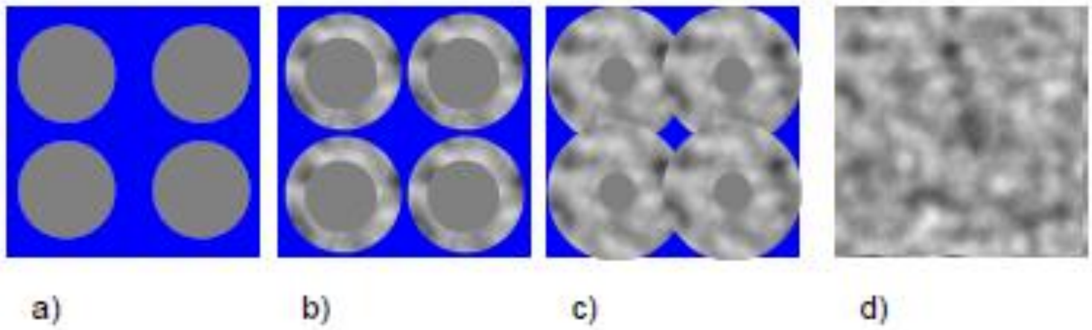


Figure 2.15: Influence of hydration on cement setting (Swan, n.d.)

Picture (a) shows the cement particles in water before the hydration starts. In (b) the product of hydration starts growing on the surroundings of the cement particle. Nelson *et al.* (1990) refer to this step as the hydration of C_3S during the dormant stage where a thick gel-like layer will grow around the silicate particles. This gel-like material is impermeable, preventing more water from contacting the unhydrated silicates, and thus preventing the hydration progress. After some time, this layer becomes permeable and hydration continues. The transformation of this layer from impermeable to permeable has not yet been understood. In picture (c) the products of hydration form a solid matrix even though the hydration has not yet come to completion. In picture (d) there is no unhydrated cement particle and no residual mix water, resulting in a solid material after some time.

As setting has to do with the solidification of the paste, Roussel *et al.* (2012) explained the kinetics rigidification of cement paste based on both physics and chemical interpretations. They associate the evolution of solidification of paste to the cement paste yield stress development that depends strongly on the formation of Calcium silicate hydrate (C-S-H). Garrault *et al.* (2006) confirmed the same fact, stating that setting and the strength of cement are influenced by $C_3S_2H_3$, as well as by C-S-H and calcium hydroxide (CH), also called portlandite.

The findings of Roussel *et al.* (2012) are surprising in that they demonstrate, as shown in Figure 2.16, how most of the cementitious materials are able to develop a coagulated particles network just a few seconds after mixing, enabling the paste to resist stress even though in the dormant stage. This stage has been overlooked by many researchers in much of the literature where rheological measurements are done after a few minutes, subsequently missing important information of rheological behaviour during the dormant stage. Vikan (2005) confirmed the same fact, demonstrating this by monitoring the heat rate of heat evolution over time of hydration so that the initial setting time of cement paste corresponds to the end of this stage.

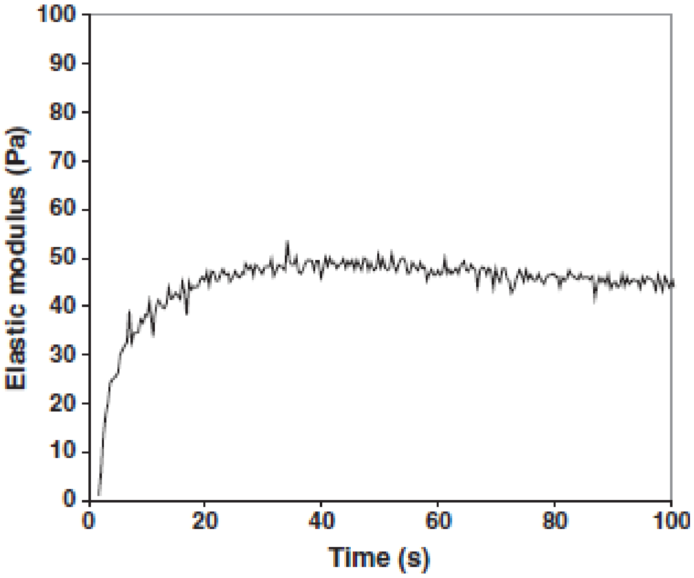


Figure 2.16: Stress development of cement paste at w/c = 0.35 (Roussel *et al.,* 2012)

They further suggested that everything starts with the nucleation of CSH in the dissolution stage that turns the colloidal interaction of cement particles into a rigid interaction**.** Roussel *et al.* (2012) concurred with the model suggested by Swan (n.d.)**,** expanding this concept by describing the structure development of cement paste as shown in Figure 2.187. They proved that at the end of mixing, cement particles are dispersed. Within seconds, the CSH nucleation starts growing on cement particles at pseudo-points of contact and due to colloidal attractive forces, these particles flocculate, forming an interactive particle system susceptible to resist stress. The CSH nucleation locally transforms the colloidal interaction between particles into CSH bridges causing, macroscopically, an increase of the elastic modulus. After several tens of seconds, the particles' interaction is purely ensured by CSH bridges, as illustrated in Figure 2.178. The increase of the rigidity will thus depend on the number and size of CSH bridges created between particles that define specific aggregate percolation paths.

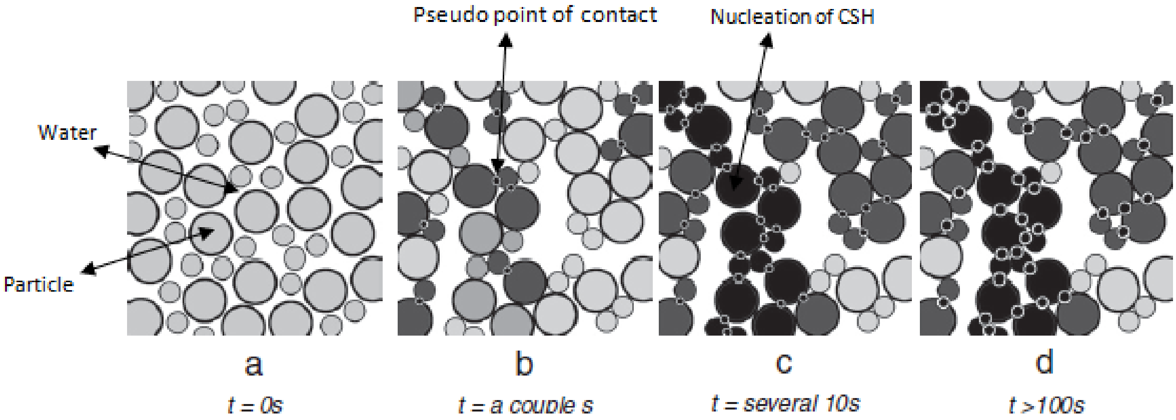


Figure 2.17: Development of cement paste rigidity: (a) cement particle dispersed in water; (b) nucleation of CSH and formation of interacting particle system; (c) formation of rigid network in the material; and (d) the size and number of CSH bridge increase and elastic modulus increases (Roussel et al., 2012)

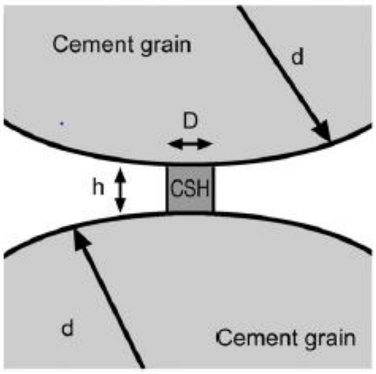


Figure 2.18: CSH bridge between two cement particles (Roussel et al., 2012)

Hall (2009) demonstrated the formation of CSH during the four stages of C_3S hydration, as in Figure 2.19.

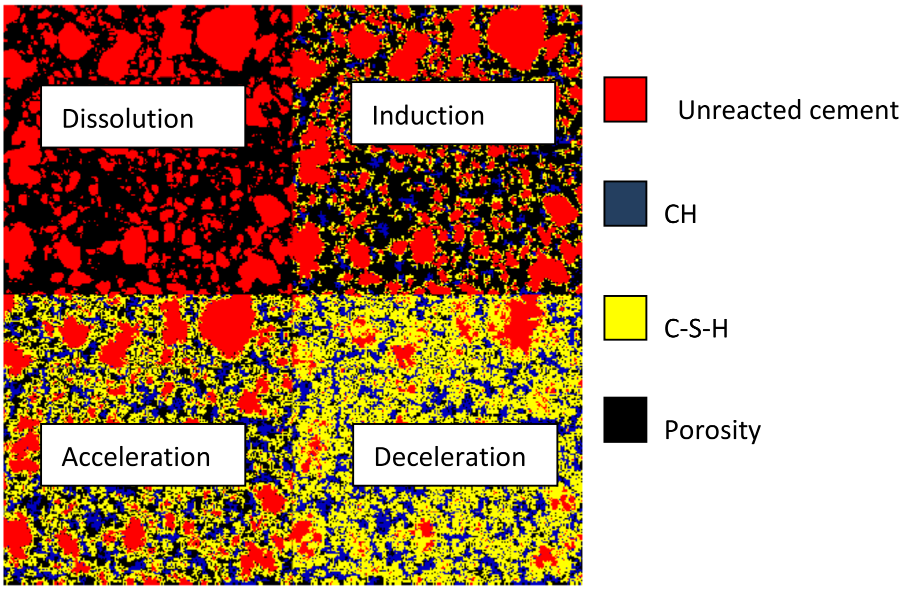


Figure 2.19: Formation of CSH during C_3S hydration (Hall, 2009)

Struble and Wei-Guo (1995) explained the impact of cement setting on rheological behaviour of cement paste. They defined the rheological parameters involved during setting and associated the yield stress and plastic viscosity of cement paste to this transformation. They then stated that the plastic viscosity depends on the volume of solid particles and their packing density, whilst the yield stress indicates the strength of the interparticle attractive forces responsible for coagulation, so that hydration increases the plastic viscosity and the yield stress. Yield stress is deemed to be the most sensitive to hydration reactions because the products of hydration cause cement particles to bond together or increase the number of interparticle links. They therefore suggested that the setting corresponds to the development of the cement paste yield stress. The yield stress gives an idea of how the cement develops its strength over time.

Since this strength development depends on the time, a single value of yield stress will never be sufficient to characterise the evolution of rheological properties of cement paste. However, with setting as an empirical parameter, researchers focus on associating chemical and physical properties of cement paste on setting, rather than trying to provide evidence through direct experiments that would associate this phenomenon to specific hydration reactions.

For this reason, a few approaches have been used to quantify the initial and the final setting time of cement, such as the one used by Sant *et al.* (2008). In order to link the intrinsic changes undergone by cement paste to setting, they evaluated the change of cement paste yield stress over time and determined three points along the yield stress growth, as illustrated in

Figure 2.20. Point A indicates the initial yield stress a few minutes after first contact with water; Point B indicates the time interval at which the yield stress significantly increases; and Point C depends on the ability of the measurement instrument used. They found that in the interval AB, the cement paste was viscous fluid exhibiting little resistance to the shearing, while the region BC showed an increase in yield stress, with the material becoming more solid-like due to the development of a solid network of particles within the paste. At this stage, the placement of cement paste wouldn't be feasible. They therefore refer to Point B as the *initial setting time*.

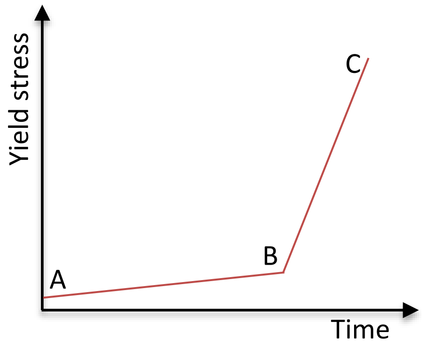


Figure 2.20: Yield stress development over time of cement paste (Sant *et al.*, 2008)

Struble and Wei-Guo (1995) observed the same behaviour of yield stress, where it first increases slowly and thereafter more rapidly. They discovered that this rapid increase occurs at the end of the dormant phase and corresponds with the initial setting of cement.

Similarly, other researchers used empirical testing methods to quantify the effect of some cement characteristics on the cement setting. This setting time measurement includes, as described by Lootens *et al.* (2009), the Vicat needle, penetrometers of various shapes, proctor needle and a Hilti nail gun. For instance, during their studies concerning rheological changes and setting of cement paste, Struble and Wei-Guo (1995) reported that cement pastes with low content of w/c ratio had a shorter initial setting time. Similarly, Nelson *et al.* (1990) and Pedrajas *et al.* (2014) mentioned that cements with low concentration of C_3S and C_3A were experiencing long hydration times resulting in great initial setting time, thereby allowing the cement to be pumped for a long period of time.

2.3.6 Interaction between cement paste and superplasticiser

Superplasticisers

Dispersive admixtures were first used in the 1960s by German and Japanese construction companies with the development of sulphonated melamine formaldehydes and analogous naphthalene derivatives. Chandra and Björnström (2002) reported the progress made in developing these admixtures, classifying them in different generations such as lignosulfonic acid (LS), melamine formaldehyde sulfonic acid (SMF), naphthalene formaldehyde sulfonic acid (SNF) and polycarboxylic acid (PA). SMF, SNF and PA admixtures are often referred to as *superplasticisers*. Only fairly recently a new generation of superplasticiser based on polycarboxylate ethers (PC) was developed with greater ability to improve the fluidity of concrete and reduce segregation.

Due to their effectiveness, SPs have become indispensable and are widely used in the concrete industry, particularly for SCC. They are preferred above any other dispersive admixtures because, according to Puertas *et al.* (2005)**,** they are able to do the following: make the concrete more workable and easy for placement; offer great mechanical behaviour as they use a low w/c ratio, equivalent to 20 to 30% of water reduction of the total amount of water needed; help in optimising the cement content making the SCC production cheaper; and reduce the permeability and increase the strength of concrete three times more than the strength of the conventional concrete.

Vikan (2005) stated that due to the added benefits of SPs, concrete engineers are now able to design concrete structures lasting for a 100-year service life-time with low maintenance and repair costs.

Plasticisers are distinguished from one type to the other based on their synthesis, which in turn depends on the weight and chemical configuration of the molecules of which they are comprised. Mikanovic and Jolicoeur (2008) presented a few criteria for defining a SP. Firstly, molecules need to bind to the cement particles. Secondly, these molecules have to be able to induce repulsive forces between particles of hydrated cement paste. This ability is judged based on the zeta potential induced in the colloidal system.

Polycarboxylate molecules consist of one main linear chain with lateral carboxylate and ether groups, as illustrated in Figure 2.21.

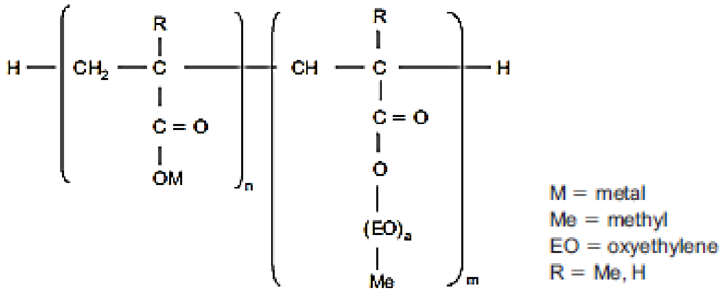


Figure 2.21: Chemical composition of polycarboxylate based superplasticiser (Puertas *et al.,* 2005)

The efficiency of polycarboxylate-based superplasticisers depends largely on the nature of the lateral carboxylate and ether groups that are responsible, respectively, for electrostatic and steric repulsion. The degree and the duration of maintaining the cement in liquid phase by this type of superplasticiser depends on the nature of its molecular structures. If the molecules have short main chains and if their lateral chains are numerous and long, the concrete will have great and long-lasting fluidity. Likewise, Puertas *et al.* (2005) mentioned that SPs with large molecular weight are greatly adsorbed and thus offer a high fluidity. SPs based on polycarboxylate reduce the water content up to 40%, allowing for the production of workable and high performance concrete. Due to these characteristics, polycarboxylate SPs are mostly used in SCC. However, these admixtures have a few drawbacks that are directly related to cement hydration.

Superplasticisers achieve their dispersion effect by two mechanisms – electrostatic repulsion and steric hindrance – as illustrated in Figure 2.22.

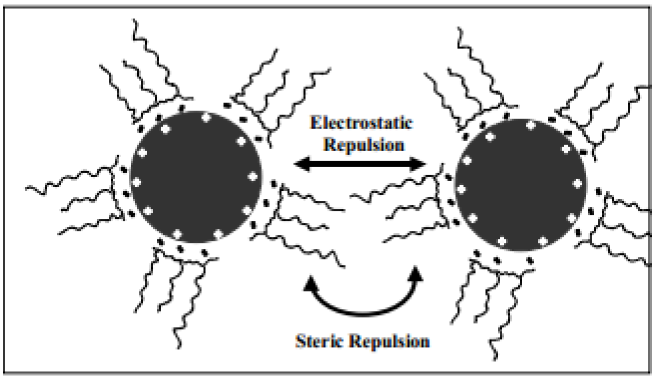


Figure 2.22: Electrostatic repulsion and steric hindrance of SP on cement particles (Hommer & von Seyerl, 2008)

It is recognised that any fractured mineral particle has two different domains that are each positively and negatively charged. Superplasticisers are negatively charged, as described by Vikan (2005), and thus will be attached to positively charged particles, turning these particles into negatively charged ones. As particles which are now charged with the same sign (negative charge) draw closer to each other, there will be an electrostatic repulsion preventing the said particles from flocculating.

Cement paste and superplasticisers interaction

Sheinn (2007) stated that the main purpose of using superplasticisers is to achieve the dispersion effect of particles in cement paste, preventing flocculation from taking place.

Superplasticisers molecules are so long and big that they wrap each and every single present powder particle in the concrete and highly charge them with a negative charge, allowing these particles to repel each other. This phenomenon allows the deflocculating and dispersion of powder particles. The mix will experience an increase in free water resulting in a higher workability of the fresh cement paste. This is confirmed by Autier *et al.* (2014) who explained that the dispersion state impacts the workability of the fresh cement paste through trapping of water in the agglomerates that increases the electrostatic repulsion effect between particles, thereby improving the flowability of the paste.

The interaction between cement paste and SP is better explained by Mikanovic and Jolicoeur (2008) who showed in their research that the dispersion of particles depends on the adsorption of SP molecules on the particles of the cement. These SP molecules prevent the particles from agglomerating. The free water is trapped between flocculants and the remaining water contributes only to the fluidification of the paste. In the discussion of their findings, Chandra and Björnström

(2002) reported that the fluidity of the cement paste is related to the cement hydration that depends closely on the cement composition and fineness.

These researchers pointed out some facts regarding cement-SP interactions that have been overlooked for a long time. They confirmed, firstly, that the particle size of SP molecules is just a few nanometres, whereas the cement particle size is up to 10 um. Secondly, the effect of SP is mainly on the surface of the hydrate cement particles. They continued to explain that as the hydration develops, the mix experiences a decrease in free water, shortening the distance between neighbouring cement hydrate particles. This situation will allow the SP molecules to either be expelled from the agglomeration or create a water flow that will serve as dilution of the polymer in the region where this activity is happening.

When the SP withdraws its molecules from the confined water, hydrated cement particles attract each other, while in the case where the SP allows for the free water to dilute the polymer molecules, hydrated cement particles repulse each other. The latter effect depends mostly on the cement composition because the effectiveness of the SP relies on the way it has been adsorbed onto the cement particles.

The introduction of SP in cement paste can potentially raise a number of problems directly related to the flow properties of the material. These are referred to as incompatibility of SP-cement interaction and are classified into two groups: problems caused by the effect of SP addition on the kinetic hydration of cement, and those caused by the adsorption of SP on cement particles. Hanehara and Yamada (1999) referred to these interaction problems as phenomena that include variation in initial slump, large slump loss or production of stiffness when using some types of cement with constant plasticiser dosage.

As an example concerning the flow variation resulting from the interaction SP-cement, they investigated the influence of different SPs on different cement types. They observed that the flow properties of cement paste prepared by adding different SPs to one cement type were fluctuating with respect to the type of SP used, and the flow properties of different cement types prepared by adding the same SP were changing according to the cement characteristics. Figure 2.23 illustrates these findings.

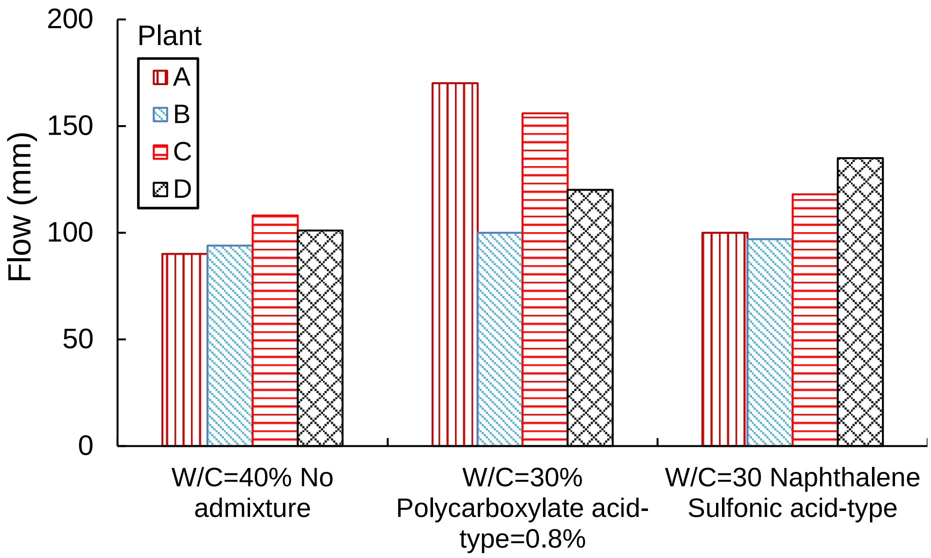


Figure 2.23: Interaction between different cement types with different SPs (Hanehara & Yamada, 1999)

Concerning the fluctuation resulting from the adsorption problem, they noticed firstly that SPs are unevenly adsorbed on cement particles depending on the mineralogy of the cement. For this reason, they found that C_3A adsorbs much more SP, followed by C_4AF, alkali sulfate, while C_2S and C_3S had less adsorption capacity. It is preferable, though, to have SP evenly adsorbed on the surfaces of cement particles in order to have a high fluidity when using a fixed amount of SP. Studies carried out by the same researchers on cements with different mineralogy compositions revealed that for some SPs, the more even the adsorption of SP on cement is, the lower the total amount of SP adsorbed on cement particles, resulting in a high fluidity. As an illustration, Figure 2.24 shows the changes induced in terms of flow by the amount of SP adsorbed on cement particles for two different SPs.

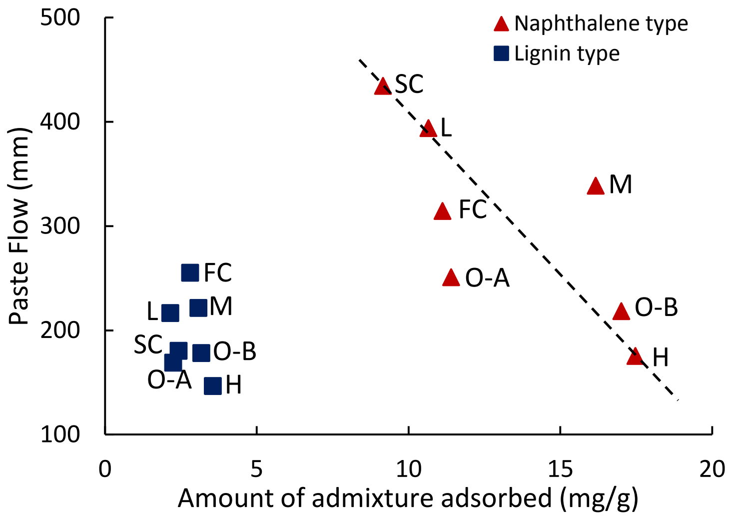


Figure 2.24: Relationship between SP adsorption on cements and paste flow (Hanehara & Yamada, 1999)

The observation of researchers on cement–SP interaction when investigating the problem resulting from polycarboxylic acid-based admixture reveals that most of the fluctuations induced depend largely on the kind of cement used.

Vikan *et al.* (2007) found that cement with low content of C_3A results in low consumption of SP, allowing the SP to remain in the solution, thereby causing a great repulsion effect between particles that leads to a retardation effect. Zingg *et al.* (2009) confirmed this, stating that with increasing content of C_3A in cement, PCE-based SPs were losing their retardation effect independently of their chemical structures. Mukhopadhyay and Jang (2009) observed that the adsorption of certain chemical admixtures depends strongly on the concentration of sulfate ions present in the cement, altering the rheological properties of cement due to the competition between C_3A and SO_3 SP adsorption. High quantities of admixtures are adsorbed and incorporated into cement hydrates if there is a low concentration of sulfate.

Consequently, the cement hydrate will lose its dispersing effect. Similarly, a small amount of admixture is adsorbed if the concentration of sulfate is too high. In the case where there is a low quantity of sulfate in the cement paste mixture, the hydration of C_3A yields calcium Aluminate hydrates which are responsible for flash setting, while in the case where there is a high quantity of sulfate, the nucleation and growth of gypsum crystals lead to a false setting behaviour. Vikan *et al.* (2007) stated that the phenomenon of cement-SP incompatibility is related to the concentration of SO_4^{2-} ions in the suspension. A high concentration of these ions allows more SP to remain in the liquid phase since they decrease the consumption of SP, resulting in high fluidification of the cement paste. They reported that during the early hydration, the compatibility of cement–SP is influenced more by the soluble alkali content in the suspension. Thus, cement with high alkali sulfates (Na_2SO_4 or K_2SO_4) will decrease the SP consumption and cause a high fluidity.The efficiency of these chemical admixtures depends mostly on the chemical composition, the SPD of the cement and water-to-cement ratio (Chandra & Björnström, 2002; Fernàndez-Altable & Casanova, 2006; Zingg *et al.*, 2009).

However, Chandra and Björnström (2002) noticed that the influence of mineralogy compound is more predominant than the physical properties of cements. They investigated four different cements in the presence of two different SPs and observed that the finest cement showed the highest fluidity in both cases, depending on the interaction of each SP with the mineralogy compounds concentration. They noticed that during hydration, the adsorption SP is influenced more by the concentration of some cement compound as described above, poisoning the hydrate products to the degree that the influence of fineness to the rheology of cement paste became insignificant.

Effect of superplasticiser on cement paste rheology

Ran *et al.* (2009) confirmed that since SPs have a significant influence on the dispersion of cement particles, so do they also have on the cement paste rheology. During their investigation on the effect of comb-like copolymer dispersants on rheological properties of concentrated cement suspensions, they found that at low dosage of SP, the paste experienced a shear thinning behaviour, and at high dosage and/or at high shear rates the paste exhibited a Newtonian behaviour. They justified this effect by demonstrating that at low shear rates, cement particles are susceptible to agglomerate or to create flocks due to the presence of attractive forces between cement particles. When the shear rate is increased, the weak link between flocks is broken into small flow units, allowing the released water entrapped within the agglomerates causing the resistance to the flow, to decrease. As the concentration of SP is increased, the paste flow behaviour moves from Bingham to Newtonian behaviour.

They emphasised the fact that there is a critical concentration of SP for each cement paste mix that is the value above which the viscosity of the cement paste remains almost unchanged. Other researchers referred to this critical value as the optimum value of SP (D’Aloia *et al.,* 2004).

A similar investigation was carried out by Agarwal *et al.* (2000) whose results proved that regardless of the type of superplasticiser used, the fluidity of the cement paste is greatly influenced. These findings led them to suggest that the measurement of viscosity can help in determining the effectiveness of a given superplasticiser. However, they demonstrated that each type of superplasticiser affects the viscosity of the paste differently, confirming that the optimum dosage of SP varies from product to product.

Koehler (2007) summarised his research concerning the effect of different admixtures on different types of cement by reporting that the polycarboxylate-based high-range water reducer admixtures (HRWRAs) decrease both the yield stress and the plastic viscosity to values near zero at critical dosage. Different researchers such as Bellotto (2013) and El Barrak *et al.* (2009) worked on different topics concerning cement paste and confirmed the same fact, pointing out the major role that SPs play in cement paste yield stress variation. They all explained the phenomenon by the fact that electrostatic and steric effects of SP move the solid particles in the paste apart, thus preventing the flocculation taking place, causing the yield stress values to drop.

Zingg *et al.* (2009) observed that the molecules of polycarboxylate-based SP were more adsorbed on C_3A, C_4AF, gypsum and their hydration products. This retarded the hydration of C_3S that could only start after two hours of hydration for some cements. Consequently, the formation of CSH and CH was delayed as well, resulting in low yield stress development.

Sheinn (2007) suggested that it is very important to use SP at its *saturation dosage* (defined by Schwartzentruber *et al.* (2006) as the value beyond which an increase in SP content doesn't significantly improve the flowability of the material) because if the dosage of superplasticiser is higher than the required dosage, there will be a lot of free water that can possibly alter the workability and strength of the fresh and hardened concrete. For SCC production, Haldenwang and Fester (2013) suggested that the correct dosage of SP is that which decreases the yield stress and the viscosity of concrete in such a way that the concrete is not too viscous 'sticky' or does not segregate. Figure 2.25 illustrates this rheological requirement in order to produce an optimum SCC.

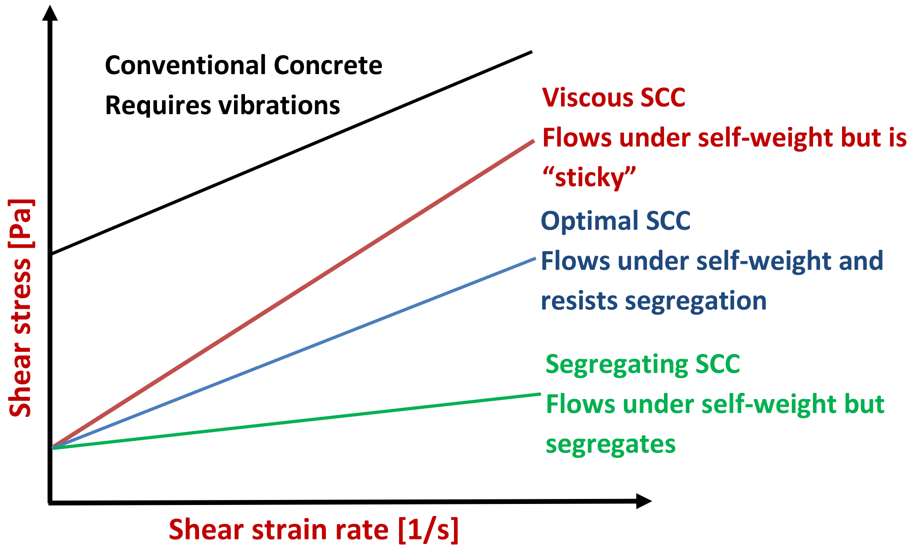


Figure 2.25: Effect of SP on rheological parameter of cement paste to produce optimum SCC

The influence of admixtures including SP on cement paste thixotropy was evaluated by Quanji (2010) who found that SP decreased the area of the hysteresis loop, while other admixtures such as VMA increased the thixotropic area.

2.3.7 Measurement of cement paste rheological parameters

From the above it can be seen that SPs affect the flow behaviour of cement paste. There are eventual incompatibilities resulting from cement paste–SP interaction that may occur, making it difficult to predict the rheological behaviour of SCC. It is, therefore, very important to select a reasonable admixture concentration for an optimum SCC by measuring the cement paste rheology. Since rheological parameters of cement paste are sensitive to the incorporated admixtures, their evaluation would be enough to give a full picture of the compatibility about cement–admixture interaction (Mukhopadhyay & Jang, 2009).

Banfill (2006) suggested that the effect of admixtures and other variables on concrete may be evaluated by small scale tests using cement paste. Previous studies concerning the assessment of SCC rheology have employed various techniques to investigate relevant rheological properties (Fernàndez-Altable & Casanova, 2006). Rheological characterisation of SCCP can be done in two ways: either by empirical tests or by rheological experiments.

Empirical tests

This testing procedure comprises mostly the *spread flow* (mini cone) that is related to the yield stress of the cement paste, the *flow time* (Marsh cone) that indicates the viscosity of the paste and the *inclined plane test* that calculates the static yield stress which helps to estimate the thixotropy of the material. Figure 2.26 illustrates the spread and the flow time methods.

The *slump flow* test consists of a truncated cone of 10 and 7 cm diameters and 6 cm height. The cone is filled with the cement paste and placed on a glass plate. After being lifted up, the cement paste flows onto the glass plate and the diameters in two perpendicular directions are measured. The final diameter is the mean of these orthogonal diameters. The time required for a 400 ml volume of cement paste to flow through a nozzle of 8 mm diameters is measured, as this gives an indication of cement paste viscosity. The cement with low fluidity is the cement that takes longest to flow through the nozzle (Schwartzentruber *et al.*, 2006; Khayat *et al.,* 2012).

The *inclined plane* method consists of pouring a certain volume of fresh cement paste on a horizontal plate whose roughness is known. One of the edges of the plate is progressively lifted up until a certain height is reached and the paste starts flowing, as described in Figure 2.27. The angle corresponding to this critical height is is used to calculate the static yield stress with respect to the Equation (2.27):

$$\tau_{0rest} = \rho.g.h.\sin\alpha \tag{2.27}$$

In Equation 2.27, ρ is the density of the paste; g the gravitational acceleration (9.81 m/s^2); h the characteristic height (mm) of the slumped sample; and α the critical angle expressed in degree of the plane at the time at which the paste starts flowing. A minimum of four tests after different resting times is enough to evaluate the rate of static yield stress increase that gives an idea about the thixotropy of the cement.

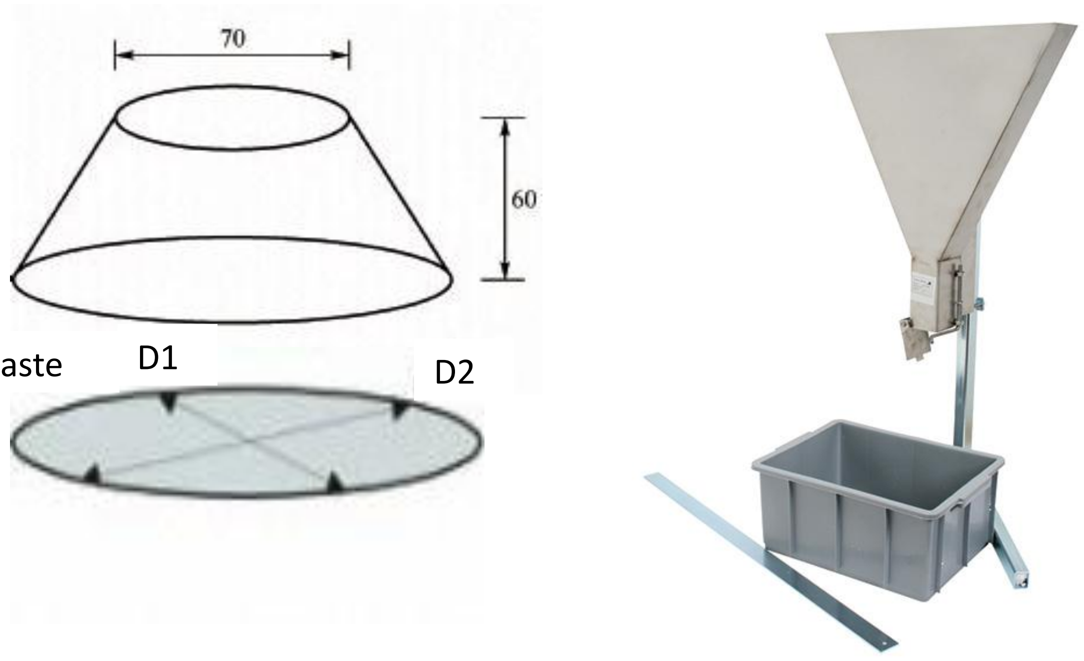


Figure 2.26: Empirical tests for cement paste rheological behaviour (Koehler, 2007)

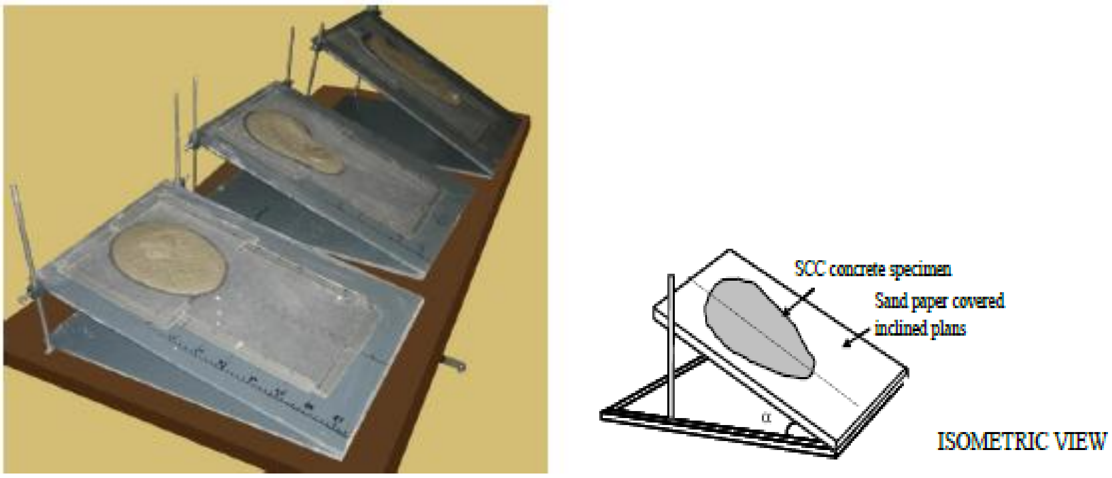


Figure 2.27: Empirical test for rate of increase in static yields stress (Khayat *et al.,* 2012)

However, these empirical methods have been criticised by many researchers as they only provide limited information concerning the flow properties. Quanji (2010) stated that these test methods provide limited information of cement paste flow because the properties to be evaluated are only partially measured. That is, he insisted that a more detailed approach that could better describe and predict the rheological properties of concrete must be established. Ferraris *et al.* (2001) reported that the spread test is not always representative of the cement paste workability as it does not generate enough detail to characterise the flow properties. Mukhopadhyay and Jang (2009) demonstrated that two different pastes can have the same spread but behave differently during placement, as shown in Figure 2.28.

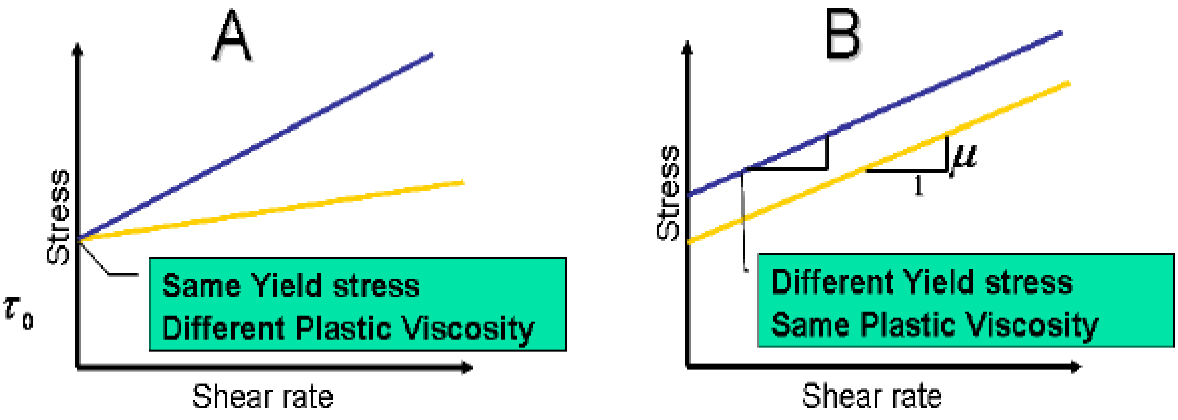


Figure 2.28: Two different cement pastes with same yield stress but different viscosity (Jang, 2009)

Banfill (2006) revealed the deficiency of these tests by showing that their matrix allows the measurement of the material properties to be viable only under certain conditions. These tests relate material property to a specific shear rate caused by an application of a single force referred as to *shear stress*. Since, for instance, the apparent viscosity of some material changes with respect to the conditions to which it is subjected, these tests can't be suitable for non-Newtonian fluids such as cement paste, yet can render good results for Newtonian fluids. In reality, cement paste is subjected to different shearing mechanisms, so Banfill (2006) suggested that the measurement of rheological properties be done under different conditions as per the two-points method developed by Tattersal who used the Bingham model for cement paste and concrete characterisation.

Fernàndez-Altable and Casanova (2006) demonstrated how the interpretation of the results obtained from this testing technique are limited due to the fact that the shear rate at which the fluid subjected is firstly, unknown, and secondly, changing over the course of the experiments.

Rheological approach

Contrary to the empirical test method available, rheometry is still the only method that can measure, at the same time, the yield stress and the viscosity of cementitious materials based on the combination of the applied shear history (Quanji, 2010)**.** The characterisation of the fluid is done by using appropriate rheological models as described in section 2.2.8.

- ***Measurement of thixotropy***

It is very important to determine the rate of rebuilding of cement paste because the workability of SCC, including the segregation resistance, drop in lateral pressure after casting and bond strength in multi-layer casting can be affected by this (Rahman *et al.,* 2014; Khayat *et al.,* 2012). Cement paste thixotropy can be determined either by structural build-up or breakdown, the latter consisting of subjecting the material to different shear rates, and the former consisting of measuring the material at different resting times.

There are more techniques available to estimate the thixotropy of suspension material. The most popular measuring technique throughout the literature relating to cement paste remains the hysteresis loop (Quanji, 2010; Mewis & Wagner, 2009)**.**

Mathematically speaking, *hysteresis* is defined as a path that describes a phenomenon based on its historical behaviour. And *loop* is more pronounced in mathematical models whereby the origin of one phenomenon corresponds to the end of the other. The method, therefore, makes sense and becomes applicable to cement paste or concrete since these exhibit a time-dependent stress response and are more influenced by the shear stress history (Esping, 2007).

Since thixotropy has to deal with the microstructural rebuilding of cement-based material, the shear stress history is obtained by implementing a mechanism to break the microstructural stability of the paste and closely observe its rebuilding. The shearing procedure is done in such a way that the shear rate is increased from a lowest possible value up to a pre-determined point and ramped back again to the initial value. The up and down branch on flow curve, as illustrated in Figure 2.29, is then obtained and the area between these curves gives an indication of the energy required to breakdown the microstructure. This so-called *thixotropy area* can be used to measure the thixotropy of the cement paste (Quanji, 2010).

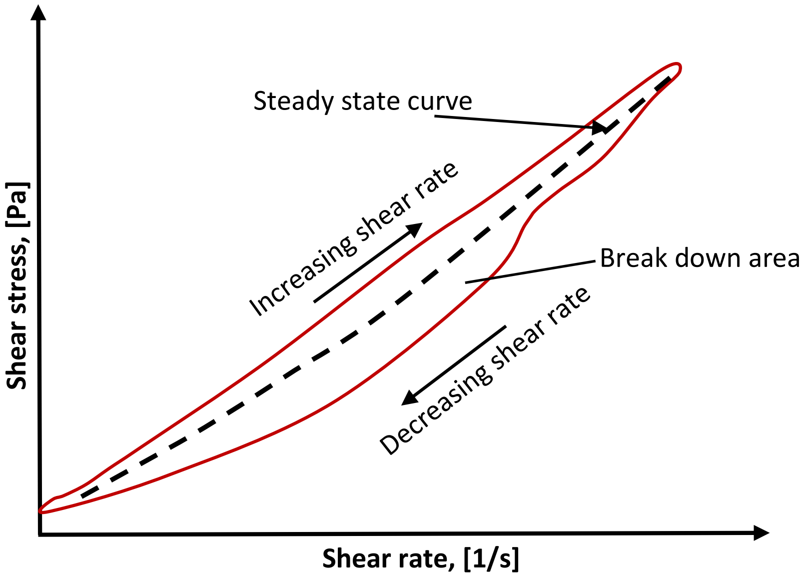


Figure 2.29: Up and down curve for thixotropy area measurement (Quanji, 2010)

Hysteresis loops can be measured at different times of rest, and corresponding curves relating to the thixotropy area to resting time of the material can be established. Quanji (2010) used this method to evaluate the rate of rebuilding of four different materials, suggesting that the slope of the curve can be an indication of how fast the material is restructuring. Khayat *et al.* (2012) used the thixotropy value at 15 minutes of rest to determine the lateral pressure exerted by SCC on the formwork and the residual bond strength in successive layers during SCC casting. It was reported by Quanji (2010) that the interacting forces responsible for flocculation of particles in the paste reach their equilibrium 15 minutes after mixing has taken place. Rahman *et al.* (2014) evaluated the thixotropy as well in intervals of five minutes, starting from one to 15 minutes resting time.

- ***Measurement of yield stress and viscosity***

The knowledge of these rheological parameters is not only useful for problems directly related to the curing process, but also during the operation and handling of SCC. For instance, challenges related to the determination of minimum pumping pressure to be applied to initiate the flow of cement paste, and the entrapment of air in SCC, require the value of yield stress to be evaluated. There have been numnerous techniques developed to estimate the yield stress and viscosity of cementitious materials. The latter can be determined either directly or indirectly.

Cement paste as a viscoelastic material exhibits two behaviours: liquid-like and solid-like behaviour. The selection of the appropriate method to measure its rheological parameters will depend on the application of the material. Banfill (2006) suggested that for flow and remoulding, the liquid phase of the paste is more relevant and a variety of rotational viscometers can be used. In the case where the cement has to be used in such a way that it doesn't have to flow under its own weight but has to stand unsupported in a pile, the solid-like behaviour is predominant.

There are many techniques available to assess the solid-like behaviour of cementitious material. Some proceed by breaking the structure, others by keeping the microstructure of the material unaffected. The direct method allows the measurement of yield stress without destroying the particles' network of the paste. Small stresses below the yield values are applied. Static and dynamic yield stresses are determined and correspond respectively to the values that show the end of the liquid phase and the beginning of the viscous phase of the material. It is, therefore, possible with this method to study the two phases of the material, especially when using the oscillatory technique. Figure 2.30 illustrates the position of these two yield stress values (Williams *et al.,* 1999).

This method implies the determination of yield stress independently of flow curve. In this case, a constant shear rate rheometer is used and the stress is increased progressively. The dynamic yield stress value corresponds to the maximum value of the shear stress at point B, while the static yield stress corresponds to point A where the curve deviates from linearity as demonstrated in Figure 2.30 (Schwartzentruber *et al.,* 2006; Esping, 2007).

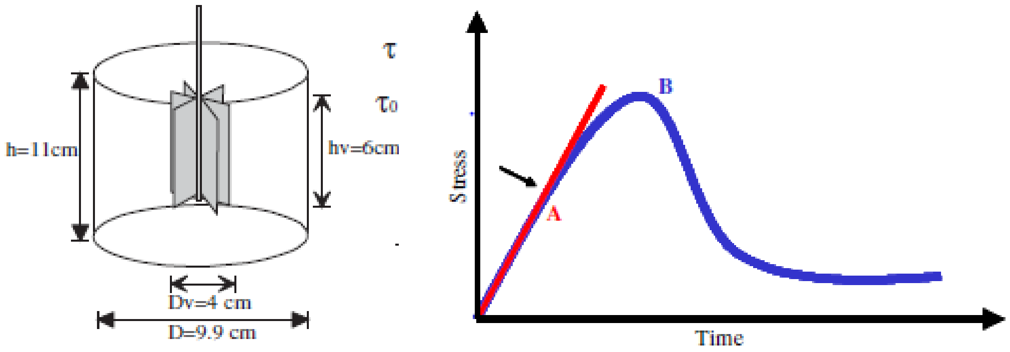


Figure 2.30: Determination of yield stress by constant shear stress rheometer A) static yield stress, and B) dynamic yield stress (Schwartzentruber *et al.,* 2006; Zhang *et al.,* 2010)

However, this technique is not widely appreciated due to some physical phenomenon like wall slip effects that are prone to occur during the measurement and thus alter the true value of material yield stress (Williams *et al.,* 1999; Assaad *et al.,* 2014). With this method, it is difficult to measure simultaneously both yield stress and viscosity. The determination of the latter requires that a supplementary test be conducted. In addition, the limitation in minimum possible torque of commercial rheometers makes this testing approach very difficult in practice. Moreover, the biggest challenge with this method is that as measurements are done under small stresses, samples can set before the measurement of the true yield has been reached, leading to an overestimated yield stress value (Zhang *et al.,* 2010).

The indirect method is used more often as it allows for measuring both yield stress and viscosity values simulaneously. This method consists of extrapolating the values of shear stress from the flow curve to zero shear rate by using rheological models. The Herschel Bulkley model is preferable and very convenient for cementitious material. With this method, the value of yield stress depends on the lowest possible shear rate used during the measurement, since the curve has to be extended to intercept the stress axis. This allows for a reduction in statistical error in yield stress evaluation, and an accurate value near zero shear rate can be determined (Schwartzentruber *et al.,* 2006; Nehdi & Rahman, 2004).

However, this method has been criticised by many researchers because the determination of yield stress is done by breaking the structure of the material whch then leads to an overestimated value of the yield stress. Progress in the understanding of rheological behaviour of cement paste allowed researchers to suggest that the dynamic yield stress could be determined from the down curve of the hysteresis loop. Banfill (2006) confirmed that measured rheological properties of cement paste are sensitive to the shear history of the sample. By considering the down branch, the structure of the material that was destroyed during the up branch is allowed to restructure during the down branch, and the lowest possible shear stress value reached is considered to be the true yield stress of the material. Thus, many researchers use the down curve from the hysteresis loop to determine both the yield stress and viscosity of the cement paste, as illustrated on Figure 2.31 (Mukhopadhyay & Jang, 2009).

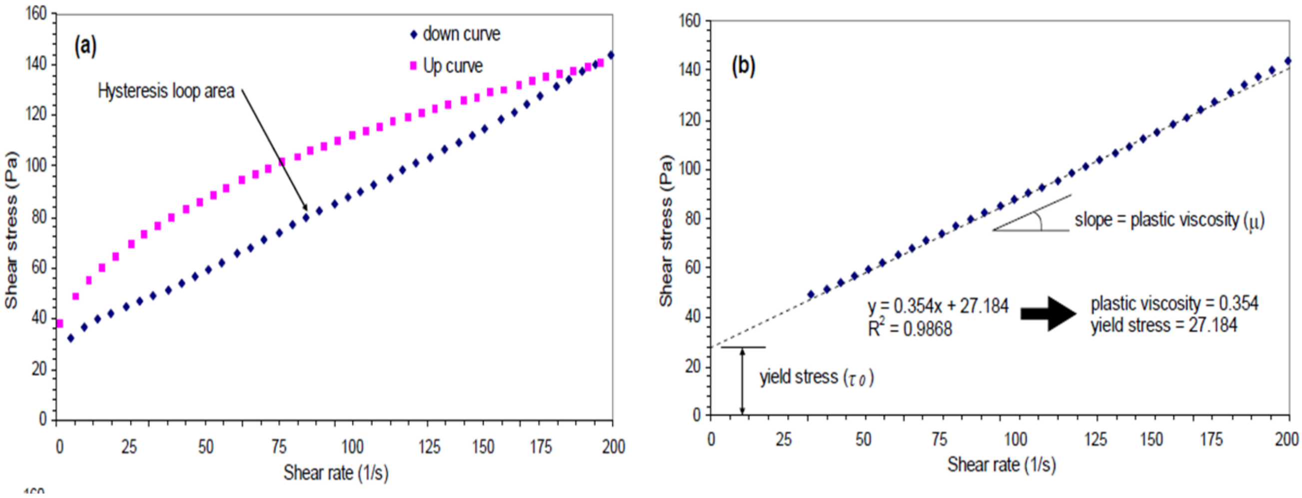


Figure 2.31: Determination of cement paste yield stress and plastic viscosity by using hysteresis loop (Mukhopadhyay & Jang, 2009)

Researchers have also questioned this manner of measuring cement paste yield stress because the approached methodology of its measurements and its rheological principle has been determined to be inconsistent. Williams *et al.* (1999) stated that though the value of yield stress obtained from flow curve measurements is reasonable, most of the time it is affected by the model, instruments used, time of measurement and the selection of shear rate range to fit the model. In addition, it has been observed that in a very small range of stresses, the magnitude of cement paste viscosity can change by several orders. This shows the difficulty of evaluating the yield stress with flow curve measurements, since the intrinsic structure of the cement paste develops with respect to the hydration kinetics comprising colloidal forces, hydrodynamics and chemical reactions. Therefore, a single value of yield stress is not enough to show this structural development within the paste (Nehdi & Al Martini, 2009; Banfill, 2006).

As addressed in previous sections, the microstructure changes within the paste are consequences of hydration kinetics that occur in the mixture. Therefore, in order to investigate the effect of the chemical and physical properties of the cement on its rheological behaviour, the correct method is that which doesn’t destroy the material and doesn’t disturb the kinetics of the cement hydration during measurement. Banfill (2006) suggested that since cement paste is a thixotropic material, these measurement conditions can only be attained in experiments where the shear rate is held constant until the equilibrium between the structural breakdown and build-up is reached within the sample.

2.3.8 Rheometry for cement paste

The challenges in studying the flow properties of cement paste when using a rheometer involve selecting effectively the test geometry, setting the appropriate gap and friction level of the shearing surface, following consistently the sampling protocol, and defining an adequate technique of rheological properties measurement (Nehdi & Rahman, 2004).

Various investigations pertaining to cement paste have been done experimentally considering all kinds of rheological measurement parameters in accordance with the rheological behaviour of interest.

Two modes of rheological measurement have to be considered: dynamic mode and shear mode Nachbaur *et al.* (2001) suggested that the fundamental information concerning the development of the microstructure and the internal forces responsible for the cement paste mechanical properties are better investigated when using the dynamic mode rheology, since measurements are done within the linear viscoelasticity domain (LVD) and so prevent the breakdown of the sample microstructure.

There is no standardised rheological measurement method to date. Hence, researchers fix the measurement parameters that suit best their own tests by minimising or eliminating factors that are prone to compromise the results.

For instance, the parallel plate is used with roughened surfaces in order to avoid slippage. The gap depends on the particle size of the cement and varies between 0.5 and 2 mm as per a study conducted by Bellotto (2013) where a 2 mm gap was used. Vikan *et al.* (2007) used a gap of 1 mm, Nachbaur *et al.* (2001) considered a gap of 2 mm, while Nehdi and Rahman (2004) used a gap of 0.7 mm.

The mixing of samples is done either by hand as per Nachbaur *et al.* (2001) or, as in other studies, by a mixer. The mixing protocol is very important in attempting to homogenise the sample by eliminating or reducing all possible agglomerates, clumps or clusters in order to wet all particle surfaces without structure breakdown (Yang & Jennings, 1995).

Williams *et al.* (1999) studied the effects of different mixing techniques on the flow properties of cement paste and found that these techniques can compensate for one another by subjecting the sample to a certain amount of pre-shear rate before starting the test. They confirmed that the pre-shearing acts as a highly controlled mixer. For instance, a sample prepared by using the hand mixing technique has a structure similar to Ross mixed paste (1500 rpm) when pre-sheared on the rheometer at 50/s shear rate. The latter was found to provide the best mixed paste with a high reduction of agglomerates.

Nachbaur *et al.* (2001) suggested that the w/c ratio be chosen with the objective of obtaining a good mixing. In cases where the effects of factors other than w/c ratio on paste are investigated, a constant w/c ratio may be selected throughout the experiment. Vikan *et al.* (2007) used a w/c ratio of 0.40% and blended the paste in a mixer for 30 seconds, and after five minutes of rest the blending started again for one minute. After 20 minutes of water addition, the test started. Fernàndez-Altable and Casanova (2006) worked with a w/c of 0.33. Their mixing was done at room temperature. The lapse between the sampling and the beginning of the test was two minutes of static hydration.

The temperature under which experiments are conducted is quite important since cement paste hydration is temperature dependent. An in-depth study of the effect of temperature on rheological properties of cement paste was carried out by Fernàndez-Altable and Casanova (2006) who found that in the range of five to 25^{o}C, rheological properties, particularly the yield stress, were not affected by temperature. They suggested that measurement be done in that interval of temperature since chemical stability of cement paste happens in that temperature range.

For dynamic mode, the pre-shearing is performed in large amplitude oscillation mode, well beyond the yield strain. Bellotto (2013) used a strain amplitude of 10% and frequency of 1 Hz lasting 30 seconds. He ran his tests using an mplitude sweep from 0.001% to 1%. Nachbaur *et al.* (2001), however, used an amplitude sweep varying from 0.01% to 10% with a frequency of 1Hz.

Vikan *et al.* (2007) used a time sweep and measured G’ and G’’ with an amplitude of 0.1% at 6Hz. For shear mode, they used a linear shear rate sweep comprising between two and 200/s. and measured the up and down cures within six minutes. They considered the down curves to determine the rheological parameters (yield stress and viscosity). Fernàndez-Altable and Casanova (2006) considered a linear shear rate sweep in the interval of zero to 100/s and used the up curve to measure the static yield stress and down curve to measure the dynamic yield stress. The entire process lasted five minutes.

Nehdi and Rahman (2004) pre-sheared the sample from zero to 70/s to cause structural break down and create a uniform condition before testing. The up and down curve was measured from zero to 50/s and vice versa for a period of three minutes. Again, the down curve was used to calculate the various rheological properties.

The selection of what mode should be used in order to study the evolution of cement paste microstructure is very controversial. According to Nachbaur *et al.* (2001) shear mode rheology can only be related to the workability of cement paste since it destroys the structure of the material. Therefore, they used the dynamic oscillatory mode. However, many researchers such as Nehdi and Rahman (2004), Vikan *et al.* (2007), and Fernàndez-Altable and Casanova (2006) have used the shear mode rheology to investigate rheological properties related to the microstructure of cement evolution.

The latter researchers studied the interaction of cement hydrate and SP on early stage evolution using the shear mode rheology. They demonstrated that the cement paste under steady flow reaches chemical stability within a certain working time of applied shear and observed a rapid growth of hydrates in the samples during the test. This evidenced the fact that shear mode doesn’t always suppress the hydration of cement paste and does not always break the structure down, as confirmed by Mewis and Wagner (2009). The investigation carried out by Bhatty (1987) on the effects of retarding admixtures on the structural development of continuously sheared cement pastes revealed different stages undergone by cement paste under continuous shear. He demonstrated (Figure 2.32) the simultaneous occurrence of structural breakdown and build-up structure of cement paste during the shearing process. Banfill and Saunders (1981) and Lapasin *et al*. (1979) conducted similar investigations on cement paste under constant shear rate and disclosed the cause of these stages.

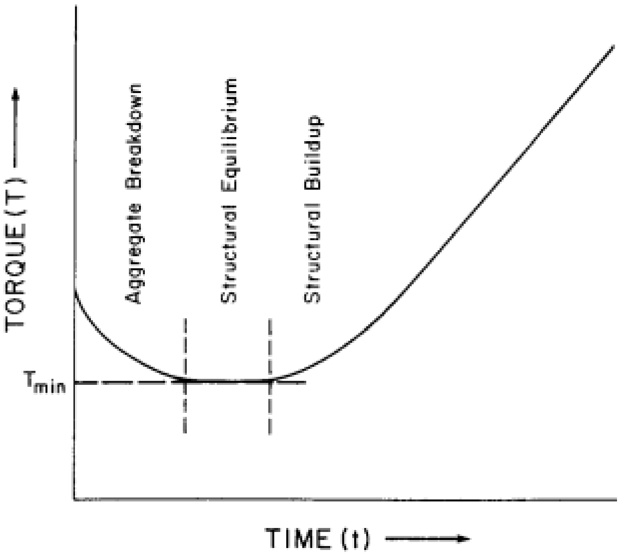


Figure 2.32: Effect of continuous shear on cement paste (Bhatty, 1987)

They emphasised the fact that the shearing of the sample is not only to orientate the particles in the suspension, but also to break down the weak bonds between particles that are formed from the end of mixing to the start of the experiment. When considering the breakdown of structure within the sample, they distinguish the microstructure of cement paste on two levels. On the one hand, there is the microstructure that has to deal with the long-range interaction between neighbouring agglomerates, and on the other hand, there is a microstructure that has to do with the short-range interactions between particles forming the agglomerates. They associate the yield stress to the first type of microstructure since the forces between agglomerates have to be overcome to initiate the flow. From the investigation carried out by Roussel (2005) pertaining to the steady and transient flow behaviour of fresh cement pastes, he concluded that under constant shear rate, the structural breakdown and structure rebuilding take place simultaneously.

2.4 Conclusion

The principles of rheology applied to different materials in terms of their rheological properties, the factors that influence their rheological behaviour and the eventual characteristics of their flow were reviewed.

Relevant rheological parameters, including viscosity and yield stress of material with constitutive equations used to quantify them, were presented.

The effect of different phases of hydration on cement paste flow properties was reconsidered.

The effect of physical and chemical characteristic of cement on the rheological behaviour of self-compacting cement paste with respect to the changes observed in its microstructure, in terms of yield stress and viscosity, were recapitulated.

The effect of cement-SP interaction on cement paste rheological properties was studied as well.

Different techniques to estimate cement paste rheological parameters were discussed and the difficulties encountered in the measurements were explained.

However, none of these methods can be used to monitor the evolution of cement paste microstructure in order to quantitatively describe the development of yield stress or apparent viscosity. Besides, rheological models cannot be used to predict the flow behaviour of cement paste without taking into account the effect of time on its structure during the hydration.

Chapter 3 Research methodology

3.1 Introduction

This project intended to quantitatively determine the impact of cement characteristics and the effect of chemical admixture on the rheological behaviour of self-compacting cement paste (SCCP). To this end, the investigation considered four different cements produced at different local factories and two commercial SPs. As cement paste is a time dependent material, it was vital to monitor the change of its rheological parameters with time. Therefore, the objectives of this research were to determine the evolution of yield stress and viscosity over time, evaluating the rate of rebuilding of these cements, both with and without SP.

The measurements of yield stress and viscosity were done in both shearing and dynamic modes. The shearing mode was comprised of both conventional flow curves as described in section 2.3.7 and the construction of flow curves, as explained in section 3.2. The dynamic mode was done in oscillatory mode, as described in section 3.3.

In addition, the evolution of cement paste microstructure was followed by monitoring the growth of its elastic modulus. A general kinetic equation of the self-acceleration type to quantitatively describe the rigidification process of cement paste was also proposed.

3.2 Measurement of yield stress and viscosity for time dependent materials by constructing the flow curves

The investigation of the evolution of cement paste microstructure seems to be very difficult when using the conventional flow curve in the shearing mode. The determination of rheological parameters by fitting the data using constitutive equations neglects to consider that cement paste is a material whose rheological properties change over time.

Generally speaking, for any rheological model used (such as the Herschel Bulkley model), the apparent viscosity for non-Newtonian fluids at a given constant shear rate is considered to be constant over time. In fact, a single value of apparent viscosity of a non-Newtonian fluid on a flow curve corresponds to the viscosity value of a Newtonian material that would behave in the same way as a non-Newtonian fluid at that particular shear rate. Thus, each point (for instance A and B on Figure 3.1) on a flow curve can then be joined to the origin of stress axis and the slope will give a single value of viscosity at the corresponding shear rate, as illustrated in Figure 3.1. In other words, for non-Newtonian fluid, at each constant shear rate the viscosity, should be constant over time on the flow curve (Tattersall & Banfill, 1983).

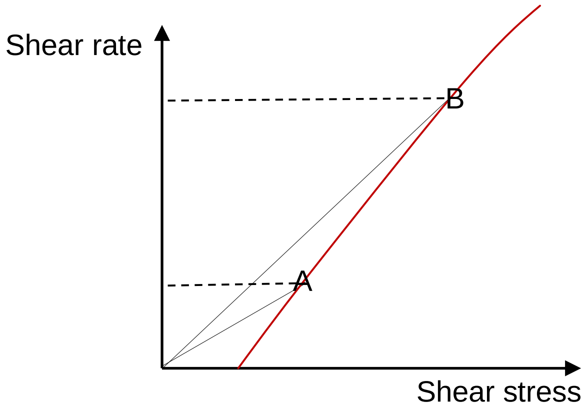


Figure 3.1: Apparent viscosity for non-Newtonian fluid with A and B specific points on the flow curve (Tattersall & Banfill, 1983)

Dealing with cement paste, a time dependent material whose viscosity evolves as the hydration progresses (Otsubo *et al.*, 1980), its rheological characterisation would therefore require that a single value of viscosity be determined at a specific point in time.

Moreover, the technical design of a rheometer to measure the rheological parameters requires that a couple of seconds be spent in between two consecutive shear rates, thus affecting the measurement since the microstructure of cement paste would be affected during that interval of time. Therefore, rheological parameters of cement paste *cannot* be measured, but *must* be deduced by constructing the flow curve.

Construction of flow curve

The main goal is to find a single value of viscosity in time at a given shear rate in order to apply the theory behind rheological models. It would be more convenient to monitor the viscosity of cement paste at a constant shear rate over time. At this shear rate, at each particular point in time, a single value of viscosity is obtained; the corresponding stress can then be calculated. This implies that at each point in time, the yield stress of the cement paste can be determined by giving information concerning the cement paste microstructure development.

The viscosity function can be defined then as follows in Equation 3:1:

$$\eta = f(t) \tag{3.1}$$

At instant t_i a corresponding η_i can be obtained for each constant $\dot{\gamma}_j$ (*j* number of considered constant shear rates) and establishing:

$$\eta_i = f(\dot{\gamma}_j) \tag{3.2}$$

So that,

$$\tau_{ij} = \eta_i . \dot{\gamma}_j \tag{3.3}$$

Taking into account the effect of yield stress and characterising the cement paste by Hershel Bulkley model:

$$\tau_{ij} = \tau_{yi} + \eta_i . \dot{\gamma}_j^n \tag{3.4}$$

The yield stress can now be defined at each point in time, and the function:

$$\tau_{y_i} = f(t_i) \tag{3.5}$$

Equation 3.5 gives the yield stress development of cement paste over time. Note that the plastic viscosity evolution is deduced as well from Equation 3.4 when $n = 1$ (Bingham model).

From the rheometer, viscosity-time sweep can be measured at different constant shear rates:

$\dot{\gamma}_j \; with \; j \equiv [1,2,3 \ldots j]$

Note that the subscript j depends on the rheometer sensitivity and limitations. This can have values such as 0.1 s^{-1}, 0.2 s^{-1}, 5 s^{-1}, 10 s^{-1}…

The development of this approach considered that the structure and the hydration of cement paste were not affected by the shearing process. However, this assumption may not be correct. Therefore, the effectiveness of this technique could be proven by the fact that the trends of yield stress or viscosity values would be different from one cement to the other, depending on their characteristics. The validation of these assumptions would be checked in measuring these rheological parameters in dynamic mode, disturbing neither the microstructure nor the development of the cement paste hydration.

3.3 Measurement of cement paste yield stress in dynamic mode

This technique was used to estimate rheological parameters in a different mode than shearing, providing relevant information on the continuous changes of cement paste structure that occur during hydration (Nehdi & Al Martini, 2009). The method aids in investigating both the elastic and viscous behaviour of cement paste (Min *et al.,* 1993).

Since cement paste is sensitive to the shear history, estimation of yield stress has always been a difficult task (Struble & Leit, 1995). Consequently, this technique was adopted in cement paste studies due to the drawbacks presented by the evaluation of yield stress by conventional flow curves (Nehdi & Al Martini, 2009; Struble & Leit, 1995).

Oscillatory shear testing is a non-destructive method as it does not destroy the structure of the material and estimates the yield stress by depicting the shift point from cement paste elastic state to its viscous state (Nehdi & Martini, 2009). Thus, the sample is subjected to a sinusoidal shear stress and the corresponding strain is measured.

The applied oscillatory stress is expressed as Equation 3.6:

$$\sigma = \sigma_0 \cos \omega t \tag{3.6}$$

For ideal elastic solid materials, the resulting strain is in phase with the stress and defined as follows:

$$\gamma = \gamma_0 \cos \omega t^* \tag{3.7}$$

While for a viscous liquid, the resulting stress is 90º out of phase with the stress, expressed by:

$$\gamma = \gamma_0 \cos\left(\omega t^* - \frac{\pi}{2}\right) \tag{3.8}$$

For cement paste as a viscoelastic material, the resulting strain can be defined as follows:

$$\gamma = \gamma_0 \cos\left(\omega t^* - \delta\right) \tag{3.9}$$

Where σ is the shear stress [Pa]; σ_0 the amplitude of shear stress [Pa]; ω is the angular velocity [S^{-1}]; t^* is the time; γ is the strain with γ_0 its amplitude; and δ is the phase shift that determines the delay of the resulting strain compared to the applied sinusoidal stress (Chow *et al.*, 1988).

The ratio between the strain and the corresponding stress defines the complex modulus G* of the material:

$$G^* = \frac{\sigma}{\gamma} \tag{3.10}$$

However, a real material exhibits viscoelastic behaviour as discussed in section 2.2.2. Therefore, the complex modulus of a material has two components that correspond respectively to its viscous and elastic behaviour. The component that takes into account the elastic part of the material is noted by *G'* and defined by Hookean behaviour as in Equation 3.11:

$$\sigma = G^{''}\gamma \tag{3.11}$$

And the viscous part is taken into consideration by *iG"* defines as per Equation 3.12:

$$iG^{''} = i\omega\eta \tag{3.12}$$

When *G'* is greater than *G"*, the material exhibits solid-like behaviour, and when *G'* is less than *G"* the material exhibits liquid-like behaviour so that the complex modulus of a material is defined by the following:

$$G^* = G' + iG^{''} \tag{3.13}$$

G' is referred to as the storage modulus and determines the energy stored within the material, while *G"* is the loss modulus representing the energy that the material loses when subjected to stress.

Schultz and Struble (1992) demonstrated that at low shear stress, cement particles are very close to each other, making cement paste behave as a solid material. Under this condition, the microstructure of the cement paste is not disturbed and can recover elastically. As soon as the applied stress reaches a certain value, however, the particles begin separating, and the flow is initiated. This attained value indicates the end of the Linear Viscoelastic Domain (LVD), as shown in Figure 3.2.

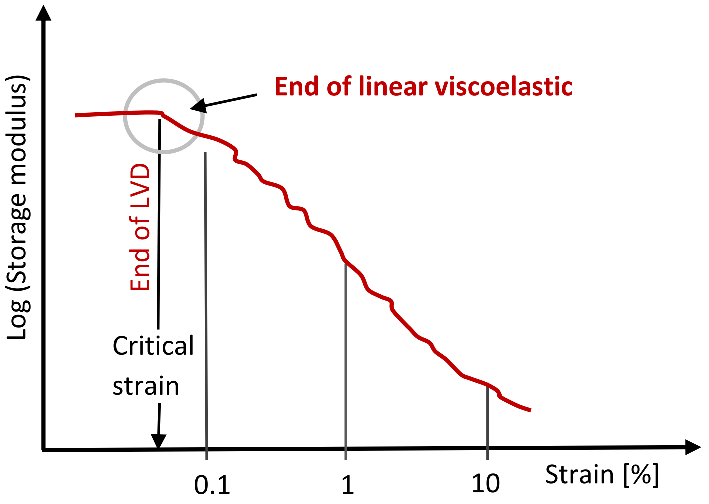


Figure 3.2: Cement paste under amplitude sweep measurements (Roussel *et al.,* 2012)

The end of the LVD region defines the region where the structure of the material is not destroyed, and is the critical strain value beyond which the interparticle forces or attractive forces between particles are overcome, and the material starts flowing. The yield stress of an individual cement corresponds to this value that can be obtained in terms of shear stress on the storage modulus versus shear strain curve, as illustrated on Figure 3.2.

This curve is sub-divided into three regions: elastic, transition and viscous zones.

In the *elastic zone* the strain is very small. The relationship between shear stress and shear strain is linear with a slope marginally equal to zero. At small shear strains, the structure of the cement paste deforms without breaking down the network (Min *et al.,* 1993).

The *transition zone* defines the region where shear strain and shear stress follow a linear curve form that indicates the beginning of the structural breakdown of cement particles (Nehdi & Al Martini, 2009). This zone defines the shift of fresh cement paste from elastic to a viscous state. The transition from the solid-like to liquid-like behaviour can occur across a remarkably narrow stress increment of about 1 Pa.

The *viscous zone* indicates that the cement paste deforms largely under the applied stress and the relationship between the shear strain and shear stress is linear (Nehdi & Al Martini, 2009).

The yield stress is then evaluated as the intersection point between the linear viscous zone and the elastic zone or the point where the storage modulus value drops.

3.4 Research design

This research was conducted on two different levels. The first level involved experimental research where samples of the various cements were tested and expected data recorded in the rheology laboratory using the appropriate instruments, as described in section 3.5.4. The second level involved a comparative study where the rheological behaviours of these cements were compared to highlight their cause, as observed in the first level of this work.

3.5 Research methodology

This section unfolds the step-by-step approach followed in the course of this work and demonstrates the relevancy of each step to the achievement of the research's goals.

3.5.1 Experimental matrix

This describes the planning of the experiments and the sequence in which they were conducted. To evaluate the effect of SP on the various cements, for each considered measurement mode, cement samples were subjected to two conditions – with and without SP –and corresponding rheological data of interest were recorded.

Figure 3.3 illustrates the tasks in detail for only one cement, but the same treatment was applied to the three remaining cements.

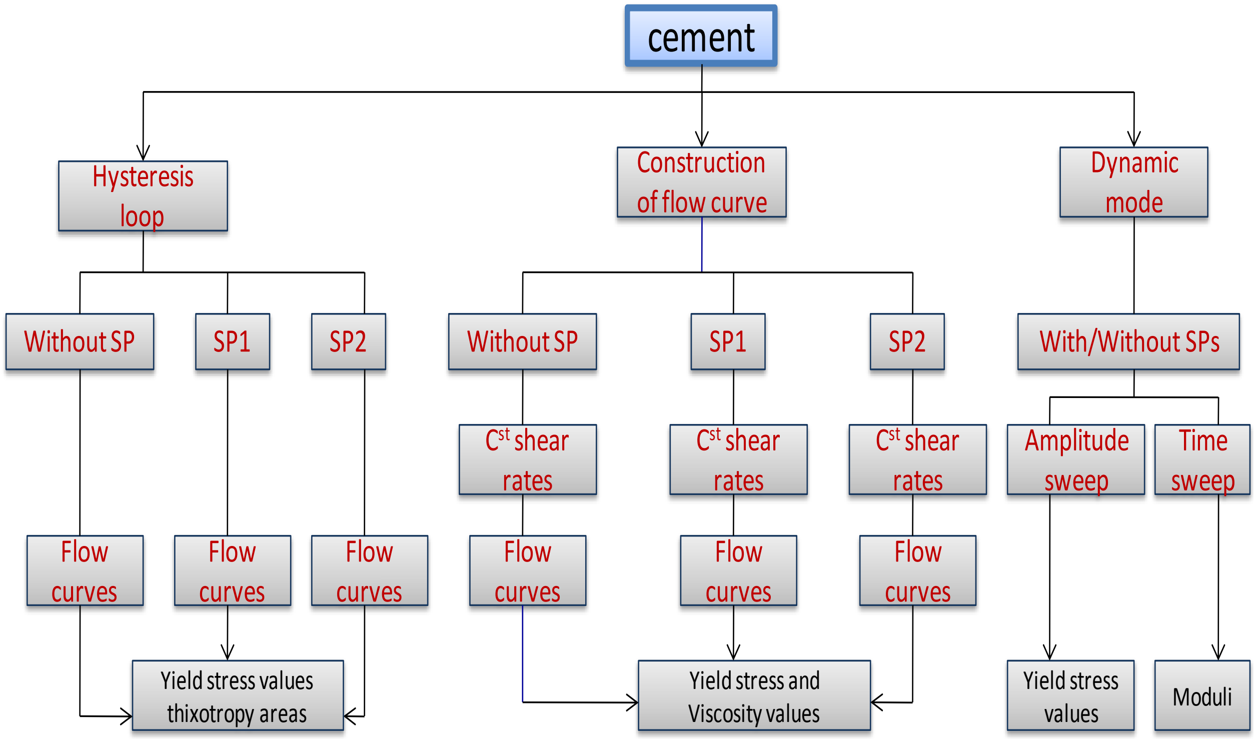


Figure 3.3: Experimental project matrix for each cement

3.5.2 Optimisation of rheological measurements

A rheometer can be used for different reasons to assess rheological behaviour of material between liquid and solid-like. In order to use the rheometer efficiently, some parameters had to be established to accommodate the material under investigation – cement paste. These measurement parameters include the gap, the temperature, the measuring time at each point, the pre-shearing rate and the duration of measurement.

Different tests were conducted to discover the optimum measurement for each parameter. Due to the large number of parameters, the optimisation was done individually first and thereafter the combined optimum parameters were run together in order to check the effectiveness of the measurement set. Literature suggests that the gap may be ten times the largest particle size of the cement, and the temperature between 24-25 ^{0}C, since the hydration of cement happens around that temperature (Vikan, 2005).

The objective was to determine a smooth viscosity time curve within a reasonable measuring time. That is, the optimisation was done for cement without SP and the measuring time was expected to be long in the case where SP was in the mix, due to the effect of SP on cement hydration. Examples of the trials of viscosity-time curves for cements are presented in Figure 3.4. The optimum rheological measurements were set accordingly.

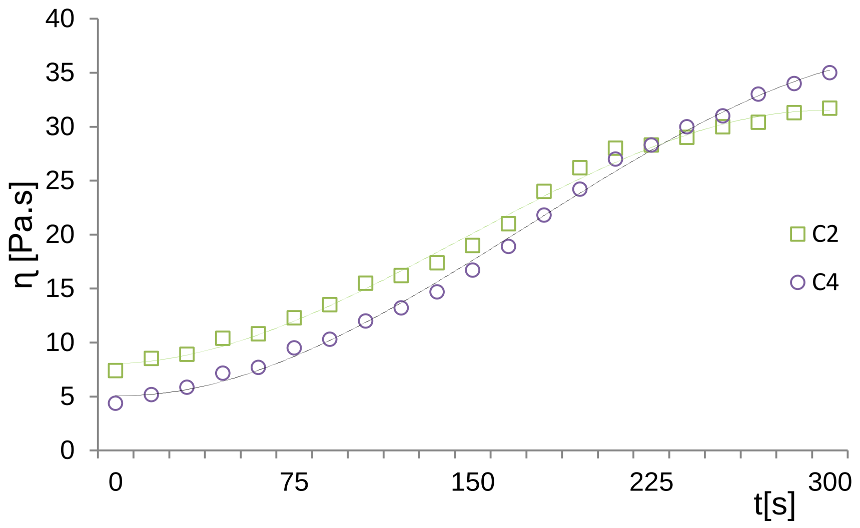


Figure 3.4: Typical viscosity-time curve for Cements C2 and C4 without SP

The optimum rheological measurements were as follows:

- Temperature: 25 ^{o}C
- Gap: 0.6 mm
- Measuring time per point: 15 s
- Pre-shearing rate: 50/s
- Time of pre-shearing: 10 s

The measuring time depended on each cement and each experiment was stopped when the sample started to set.

3.5.3 Data

Optimum value of SP

SCC implies an optimum mix design. As far as SCCP is concerned in this research, the optimisation of SP was very important. As discussed in the literature, the design of SCC is a process of looking for the ‘sweet spot’ where the cement experiences a small amount of yield stress with an adequate amount of viscosity, ensuring the flow without any form of segregation.

The yield stress is very sensitive to SP content in the mix. It is agreed that beyond the saturation dosage of SP, the yield stress decreases tremendously while the viscosity remains constant. The optimum dosage was found by acquiring the yield stress values for each various cement at different SP concentrations, while constantly observing the variation of corresponding viscosity value.

Figure 3.5 presents a typical optimisation of SPs on cement, based on the variation of yield stress against different concentrations of SP under consideration. The rest of the figures for each cement and SPs are found in Appendix A.

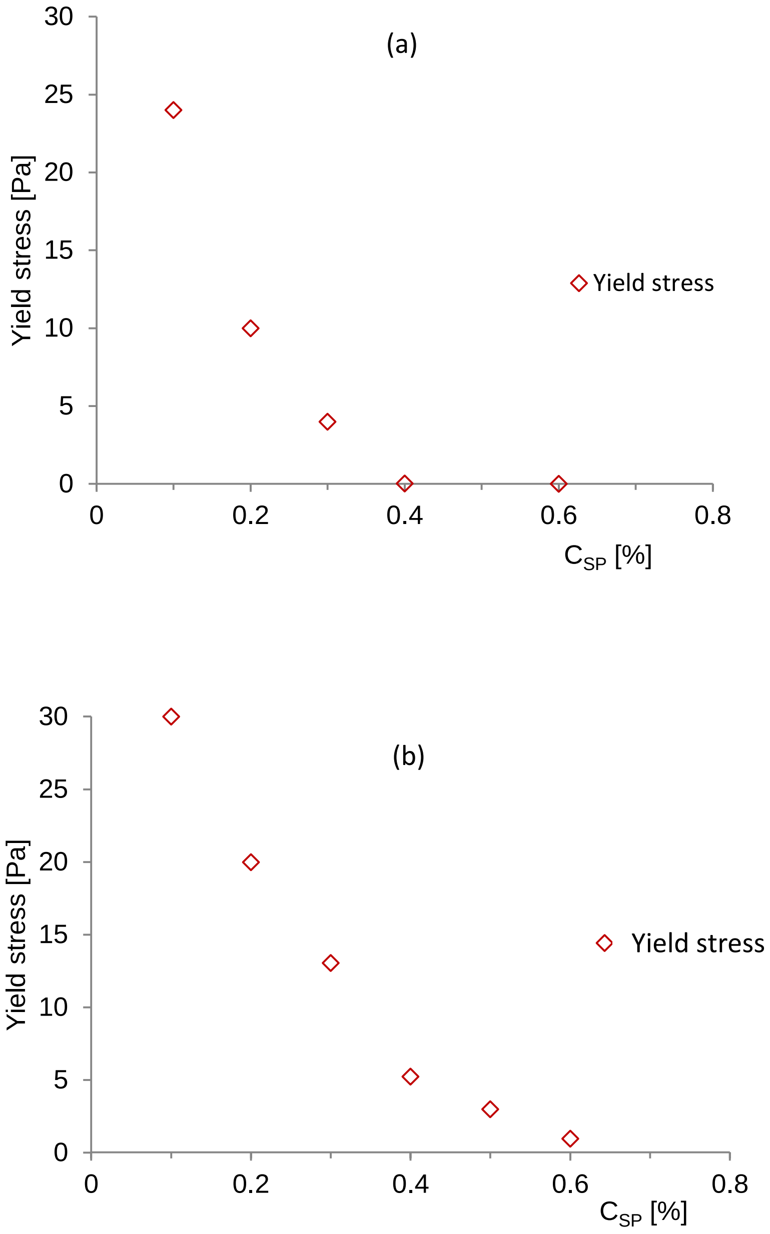


Figure 3.5: Typical yield stress change over SP1 (a), SP2 (b) concentrations for Cement C2

The saturation dosage of SP was approximated to 0.3% by weight of cement for both SPs and for all cements.

Viscosity-time

Determining the development of rheological parameters for each cement over time was crucial for answering the fundamental questions of this research. As explained in section 3.2, the only effective way to establish these parameters is by constructing the flow curve. The construction of flow curves required the measurement of viscosity over time at a constant shear rate in order to determine instantaneous values of viscosity. Viscosity curves and flow curves at particular times were deducted from these viscosity-time sweeps. To predict the trend of a curve, five constant shear rates (5 s^{-1}, 10 s^{-1}, 20 s^{-1}, 50 s^{-1} and 75 s^{-1}) were considered for measuring the viscosity-time sweep for each cement, with and without the addition of SPs.

Hysteresis loop

The up and down curve was measured for each cement at different intervals of resting time. The yield stress and viscosity values were determined by the downward branch of the hysteresis loop by extrapolation of the experimental data to zero shear rate. The extrapolation procedure was performed by linear dependence of the shear stress on shear rate (i.e. along with the Bingham equation). The thixotropy area was collected, as well at the same resting time. Plotting the thixotropy areas against the corresponding resting times provided a curve whose slope gave an estimation of the rate of rebuilding of each cement.

Amplitude sweep

A dynamic mode rheometer was used for assessing the effect of hydration on the microstructure development of the cement paste under different conditions of SP. A range of strains were considered and the storage (G') and loss (G'') moduli of the cement paste under investigation were monitored. The critical strain and the corresponding stress were determined, as explained previously.

Time sweep

The rigidification process of cement paste was followed by monitoring the growth of cement paste moduli in the LVD by subjecting the sample to a strain with constant frequency and constant amplitude smaller than the critical strain over some period of time, in an attempt to predict this growth by a general kinetic equation of self-acceleration type and the relevant constants pertaining to this model.

3.5.4 Research instruments

The rheological measurements of all cements with and without SPs were done on a MCR51 rheometer supplied by Anton Paar with temperature control as shown in Figure 3.6. The geometry used for all the measurement was a rough parallel plate suitable for dispersions such as cement paste containing particles. Figure 3.6 illustrates the measuring geometry.

Figure 3.6: Rheometer and measuring geometry used in the experimental work

One disadvantage of this measuring method, however, is that within the gap there is no constant shear gradient since the shear rate increases in value from zero at the centre of the sample to its maximum value at the edge. Phenomena such as in homogeneities, emptying of the gap, flowing off and spreading of the sample or even skin formation, can occur during the measurement. Therefore, extreme care was taken to properly fill the gap with the sample, and to trim thoroughly.

Regarding the time sweep experiments: a problem encountered when using a rheometer is that there is a certain amount of time spent from the end of mixing to the beginning of measurements that can compromise the results. In spite of care taken, additional stresses may be induced, especially during the gap adjustment, causing the measurement to be carried out on the paste that is different from the one obtained immediately after mixing. As a remedy to this issue, Bellotto (2013) suggested that the normal forces on the rheometer be monitored closely throughout the test. All material including water, cement and SPs were weighed on an electronic scale and a stop watch was used to monitor the sample preparation time.

3.5.5 Material used

Cement

Cements used in this research were produced by one company at different factories, and chemical concentrations are based on the mineralogy of the factory location.

Four cements were investigated in this project, all of them CEM I 52.5N type. Their chemical properties are presented in Table 3.1. The mineralogy compounds according to Rietveld analysis of XRD for each cement are presented in Table 3.2. Physical characteristics according to the manufacturer are given in Table 3.3.

Table 3.1: Chemical properties of cements used

Chemical properties	**C1**	**C2**	**C3**	**C4**
SiO_2 (%)	**20.8**	**21.5**	**20.9**	**22.3**
Al_2O_3 (%)	**3.8**	**4.1**	**4.0**	**4.7**
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**	**62.7**	**62.7**	**61.3**
MgO (%)	**1.2**	**3.3**	**2.9**	**2.6**
P_2O_5 (%)	**0.17**	**0.10**	**0.03**	**0.12**
SO_3 (%)	**2.33**	**2.47**	**2.81**	**2.95**
Cl (%)	**0.00**	**0.00**	**0.00**	**0.00**
K_2O (%)	**0.66**	**0.36**	**0.24**	**0.25**
Na_2O (%)	**0.34**	**0.19**	**0.15**	**0.18**
LOI (%)	**4.11**	**1.83**	**2.83**	**1.74**
Total (%)	**100.5**	**100.3**	**100.5**	**100.2**
FCaO (%)	**1.00**	**1.30**	**0.95**	**1.43**

Table 3.2: Mineralogy compound according to Rietveld analysis

Chemical properties	Chemical Formula	C1	C2	C3	C4
Calcium Silicate (C3S)	Ca_3SiO_5	59.92	50.80	52.74	54.19
Larnite (C2S)	$Ca_2(SiO_4)$	13.99	20.43	18.76	17.95
Calcium Aluminium Oxide (C3A)	$Ca_3Al_2O_6$	3.95	2.75	1.84	2.63
Brownmillerite (C4AF)	$FeAlO_3(CaO)_2$	14.54	18.46	20.49	17.15
Periclase	MgO	1.00	2.92	2.08	2.49
Lime	CaO	0.35	0.41	0.51	0.40
Arcanite	K_2SO_4	1.37	0.78	0.31	1.34
Gypsum	$CaSO_4.2H_2O$	1.62	2.74	2.92	1.29
Bassanite	$CaSO_4.0.5H_2O$	3.28	0.63	0.35	2.58

Table 3.3: Physical properties of cements used

Physical properties	C 1	C 2	C 3	C 4
Relative Density Pyc	3.05	3.03	3.04	2.99
Reported S/Surface, cm^2/g	3750	3650	4250	3850
Std Consistence, %	25.0	31.0	25.0	33.0
Initial Set, min	170	180	190	315
Final Set, h	3.25	3.75	3.75	6.00
45 μm Residue, %	11.7	0.6	3.9	1.8
90 μm Residue %	1.1	0.0	0.5	0.1
212 μm Residue, %	0.2	0.0	0.0	0.0

Superplasticiser

Two commercial SPs from the new generation of SPs supplied by different manufacturers were used in this research. SP1 is a modified vinyl polymer-based superplasticiser admixture, whereas SP2 is among the new generation of superplasticisers based on modified polycarboxylate polymers. The characteristics of these SPs are given in Table 3.4 while their molecular structure characteristics were determined as per their obtained IR spectrum in Figure 3.7. In fact, this spectrum correlates the number of carboxyl (cm^{-1}) to the absorption ability of different group function constituents of the SP to determine the respective molecular features.

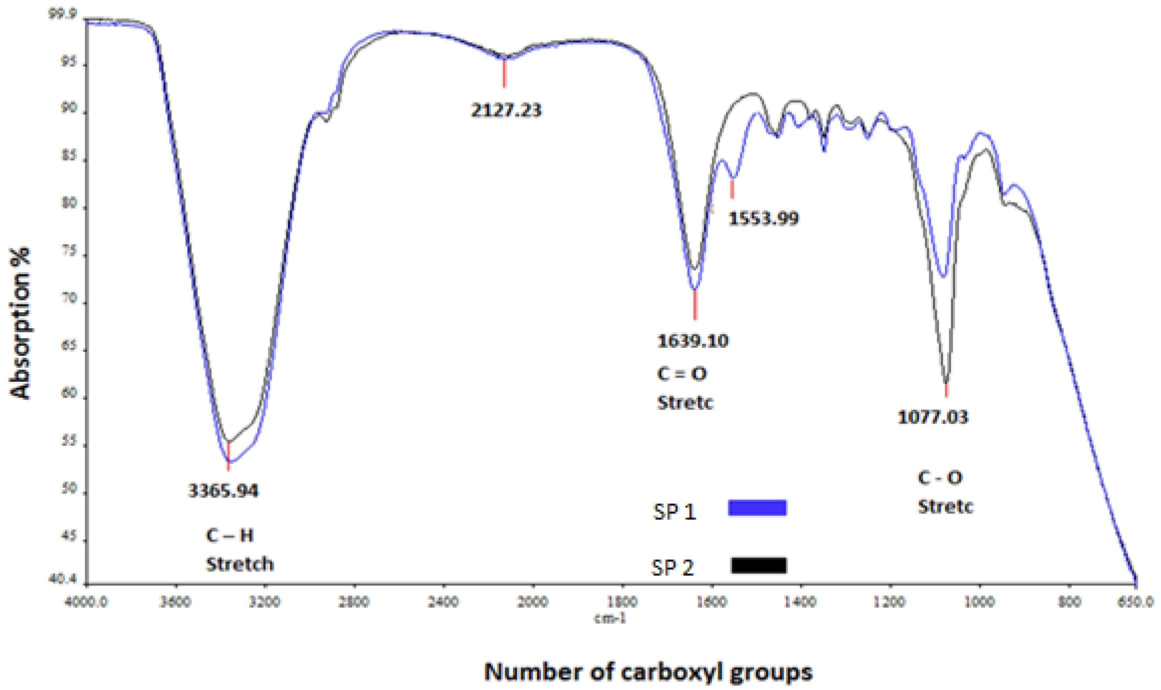


Figure 3.7: Infra red spectrum analysis for SP1 and SP2

Table 3.4: Characteristics of superplasticisers used

SUPERPLASTICISER TYPE	SP1	SP2
Characteristics		
Consistency	Liquid	Liquid
Colour	Amber	Brown-green
Density according to ISO 758 (g/cm3)	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 (Na2O equivalent) according to EN 480-12 (%)	<2.5	≤ 1.0

3.5.6 Mixing and preparing cement pastes

The main challenge in experiments with ‘living’ systems such as cement paste is ensuring the reproducibility of the measurements by bringing all the samples on the same reference line. Execution of this task depends largely on the preparation of the samples.

Experiments were carried out in a temperature and relative humidity controlled room. Deionized water was used for all the mixes at a constant water cement ratio of 0.45%, corresponding to 60.75 g of water in the absence of SP and 60.35 g in the presence of SP with the equivalent solid content.

The energy used during mixing is very important in attempting to homogenise the sample by eliminating or reducing all possible agglomerates, lumps or clusters in order to wet all particle surfaces without structure breakdown (Yang & Jennings, 1995). In this research, an intensive hand mixing method (Roy & Asaga, 1979) was used for all the cements as suggested in the work conducted by Williams *et a*l. (1999) about the effect of different mixing techniques on the flow properties of cement. They found that these techniques could be compensated for subjecting the sample to a certain amount of pre-shear before starting the test. They confirmed that the pre-shearing acts as a high speed mixer. For instance, a sample prepared by using a hand mixing technique has the similar structure to Ross mixed paste (1500 rpm) when pre-sheared on the rheometer at 50/s shear rate and provided the best mixed paste with an high reduction of agglomerates. Therefore, for the experimental works in this project, samples were mixed for two minutes in such a way that a consistent paste was obtained for all the cement paste under investigation.

For measurement of flow properties, the following procedures were used after mixing:

- For construction of flow curve, the sample was placed on the rheometer immediately by means of spatula.
- All samples were pre-sheared at 50 s^{-1} for 10 s. This time was enough for the sample to reach steady flow (Roussel, 2005).
- The measurement of viscosity-time sweep at the considered constant shear rate (5 s^{-1}, 10 s^{-1}, 20 s^{-1}, 50 s^{-1} and 75 s^{-1}) then started, with 15 s measuring time per point.
- For hysteresis loop, samples were put to rest just after mixing. Four resting times were considered between zero and 15 minutes since the internal forces in cement paste reach their equilibrium after 15 minutes. Each resting time corresponded to its specific sample (Rahman *et al.*, 2014).
- The sample was then placed on the rheometer and twenty viscosity points were considered with 10 for the up curve and 10 for the down curve.

The complete measuring cycle time was 300 s as in Banfill and Saunders (1981). The up curve was done in the interval of 0-100 s^{-1} and the down curve from 100-0 s^{-1}. The viscosity ramp was therefore 100/150 s^{-2} for both up and down curves. Figure 3.8 illustrates the variation of stress for up and down branches, and the measuring cycle time for hysteresis loop.

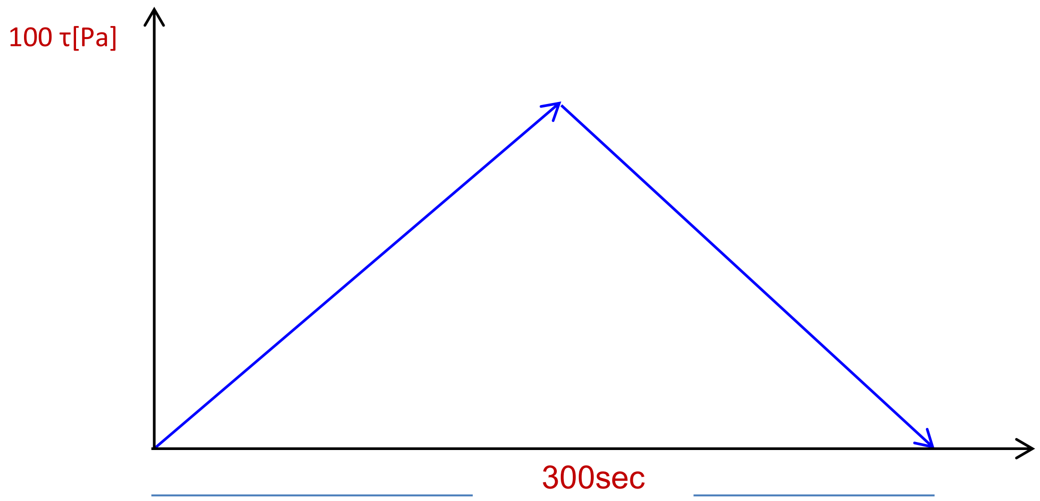


Figure 3.8: Cycle time and stress intervals for hysteresis loop measurements

For measurements of elastic properties (amplitude and time sweep) after mixing protocol the following procedures were observed:

The sample was put to rest for three minutes; thereafter the second intensive mixing was carried out for one minute instead of pre-shearing the sample in oscillation mode. The amplitude sweep was carried out from 0.01% to 1% at constant frequency of 1Hz with an amplitude rate of $\gamma = 12x10^{-5}xe^{0.015T}$ (T instantaneous hydration time). The time sweep was from zero to 1h at critical strain of 0.06% as determined in strain sweeps tests (critical strain in order to be within the LVD).

For tests which included superplasticisers, the SP was first mixed with water before the solution was added to the cement and the above sequence was performed again. No sample was used twice. After each experiment, the plates of the rheometer were cleaned and dried with care to avoid any influence of previous samples on the subsequent test. No sleep effect was observed since after testing, all samples were fresh and did not stick to the plate.

3.5.7 Data analysis

The flow properties of cement paste with and without the addition of SPs were characterised by first constructing the flow curves. These were fitted by optimising the coefficients of the Herschel-Bulkley model by simultaneous iterations. The development of rheological parameters was obtained by plotting the instantaneous yield stress and viscosity against the corresponding time; the slope of the curves could be related to the solidification of cement paste during hydration. This process could depend on the effect of cement characteristics on the rheological behaviour of cement paste. A sharp curve indicated a fast yield stress evolution implying a rapid interaction of internal forces within the paste, while a curve with a flat slope indicated a slow yield stress evolution.

Secondly, the hysteresis loop provided, simultaneously, the yield stress and viscosity values. The thixotropy areas of cement pastes were deduced directly from the same loop. The yield stress values corresponding to different resting times for each cement with and without SP were observed to investigate the effect of hydration on cement paste rheological behaviour.

The elastic properties that give the evolution of the cement paste microstructure as an effect of cement characteristics on hydration were investigated based on the yield stress values obtained from strain sweep and the coefficients of the rheokinetic model. From these values the rate of hydration could be quantified and its effect on the microstructure development was determined. The evaluation of the rebuilding rate for each cement was obtained by plotting the thixotropic area from the hysteresis loops against the corresponding resting time. The slope of the curve gives the indication of how fast the cement restructures. A steep slope corresponds to a fast rebuilding rate while a flat slope corresponds to slow restructuration of the cement paste.

To assess the effects of chemical and physical properties of cements on their rheological behaviour, it was convenient to illustrate on one graph the followings the three things: 1) the yield stress development of all cements without SPs; 2) the viscosity development of all cements without SPs; and 3) the rate of rebuilding of all cements without SPs.

The investigation of cement-SP interaction required that the following curves be overlaid on one graph: 1) the yield stress development of all cements with SP1; 2) the yield stress development of all cements with SP2; 3) the viscosity evolution of all cements with SP1; 4) the viscosity evolution of all cements with SP2; 5) the rate of rebuilding of all cements with SP1; and 6) the rate of rebuilding of all cements with SP2.

3.6 Conclusion

The two techniques to measure rheological parameters of cement paste have been introduced. The construction of flow curves method consists of determining the yield stress based on using flow curves corresponding to different periods of agglomeration. The protocol for these measurements is that the viscosity evolution is followed in time for different constant shear rates. In this way, a set of kinetic curves is obtained. Points from all curves corresponding to the same periods of time are then extracted from the kinetic curves. This provides shear rate dependencies of the apparent viscosity for different periods of setting. Finally, all these flow curves are fitted with a suitable rheological model for visco-plastic materials that allows for determining the yield stress as a function of the time of agglomeration. It is important to emphasise that this is the only method allowing one to follow the time evolution of the yield stress.

The basic principles of oscillatory measurements for assessing cement paste elastic properties by amplitude and time sweep tests were covered. Also, the concept of non-linearity in these experiments was explained. The challenges and the sample preparation in rheometry of cement paste when using the MCR51 rheometer have been clarified and the mixing protocol defined. The characteristics of both cements and SPs used in this research were described. Also, the analysis of data was illustrated. The experimental works were done in a well-equipped laboratory of Cape Peninsula University of Technology (CPUT), managed by Flow Process Research and Rheology Centre (FPRC).

Chapter 4 Results

The evolution of rheological parameters was monitored using various techniques to estimate the yield stress and the apparent viscosity of cement pastes, as explained in the two previous chapters. The evolution of moduli was followed, also by observing their behaviour over time. The thixotropy areas were calculated for estimating the rate of rebuilding of each cement. This chapter reports the results obtained from each technique: construction of flow curve and hysteresis loop to estimate the flow properties of cement paste, as well as the amplitude sweep and time sweep data to evaluate the elastic properties of the cement paste.

4.1 Flow properties

Rheological parameters were assessed in the shearing mode by constructing the flow curves and measuring the hysteresis loop for all cement pastes.

4.1.1 Rheological parameters evaluation from constructing the flow curves

This method is based on constructing flow curves by monitoring the time evolution of the apparent viscosity at different shear rates.

Viscosity evolution

The instantaneous viscosity of each cement under constant shear rate was obtained as explained in section 3.2, with and without SPs at optimum concentration of 0.3%. Figure 4.1 shows the viscosity over time at different constant shear rates of cements without SP.

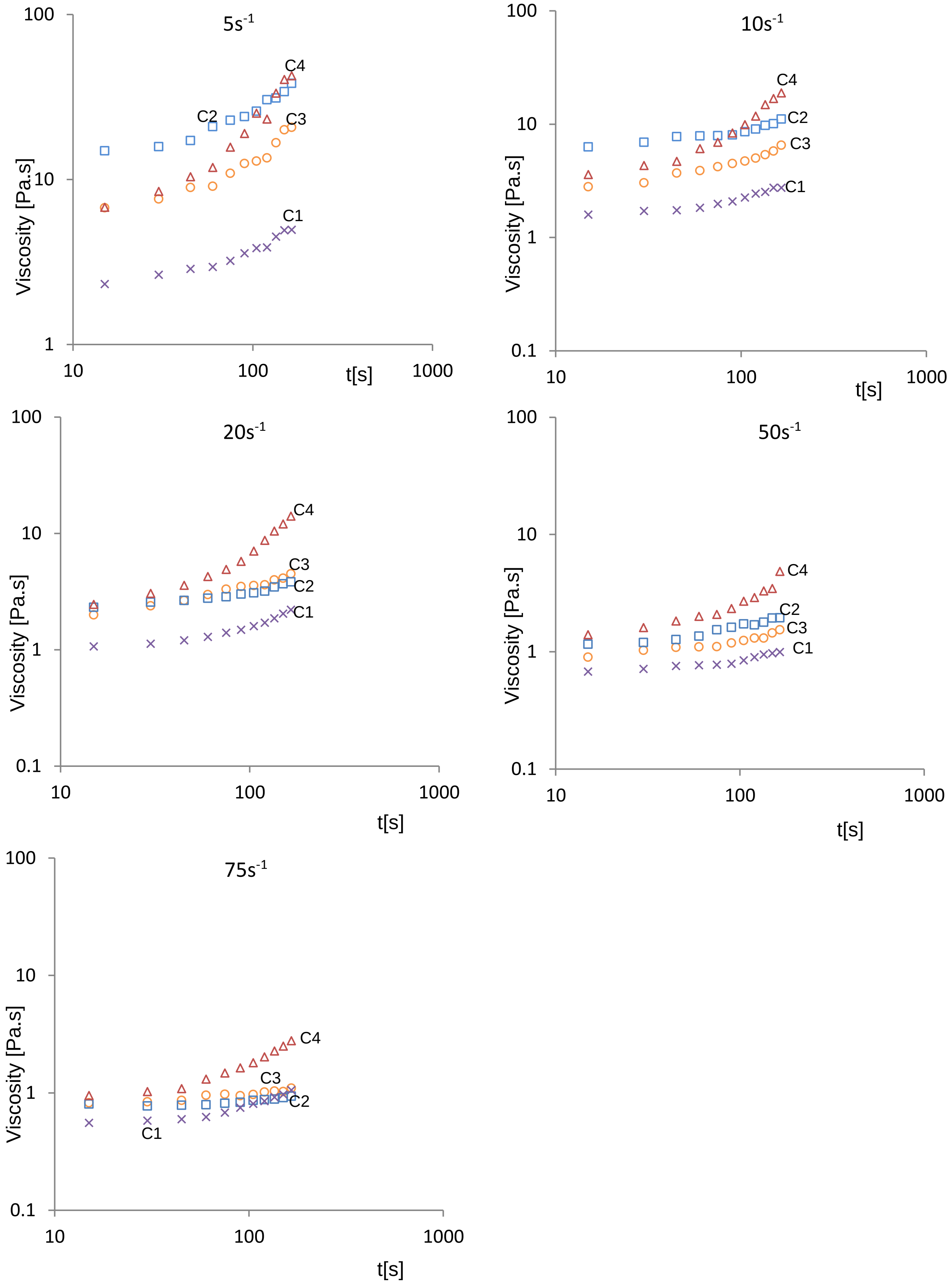


Figure 4.1: Evolution of viscosity in time at different constant shear rates of all cements without SP

It is to be expected that the viscosity of all the cements without SP would increase over time at any constant shear rate. Cement C1 exhibited the lowest viscosity for all the shear rates. Cement C4 showed a great viscosity growth with increase in hydration time. At high shear rates, the viscosity value of cements decreased significantly, but with a similar trend as at low shear rates.

The viscosity-time changes of all cements with the addition of SP1 are illustrated in Figure 4.2. It was observed that the viscosity of cements kept increasing with time, but at a different trend. At the beginning of hydration, the viscosity evolved slowly and seemed to be constant before it increased suddenly after a few seconds of hydration. As in the absence of SP, Cement C1 exhibited the lowest viscosity with a more prolonged plateau at the beginning. At high shear rates, all cements showed the same viscosity evolution as the hydration time increased.

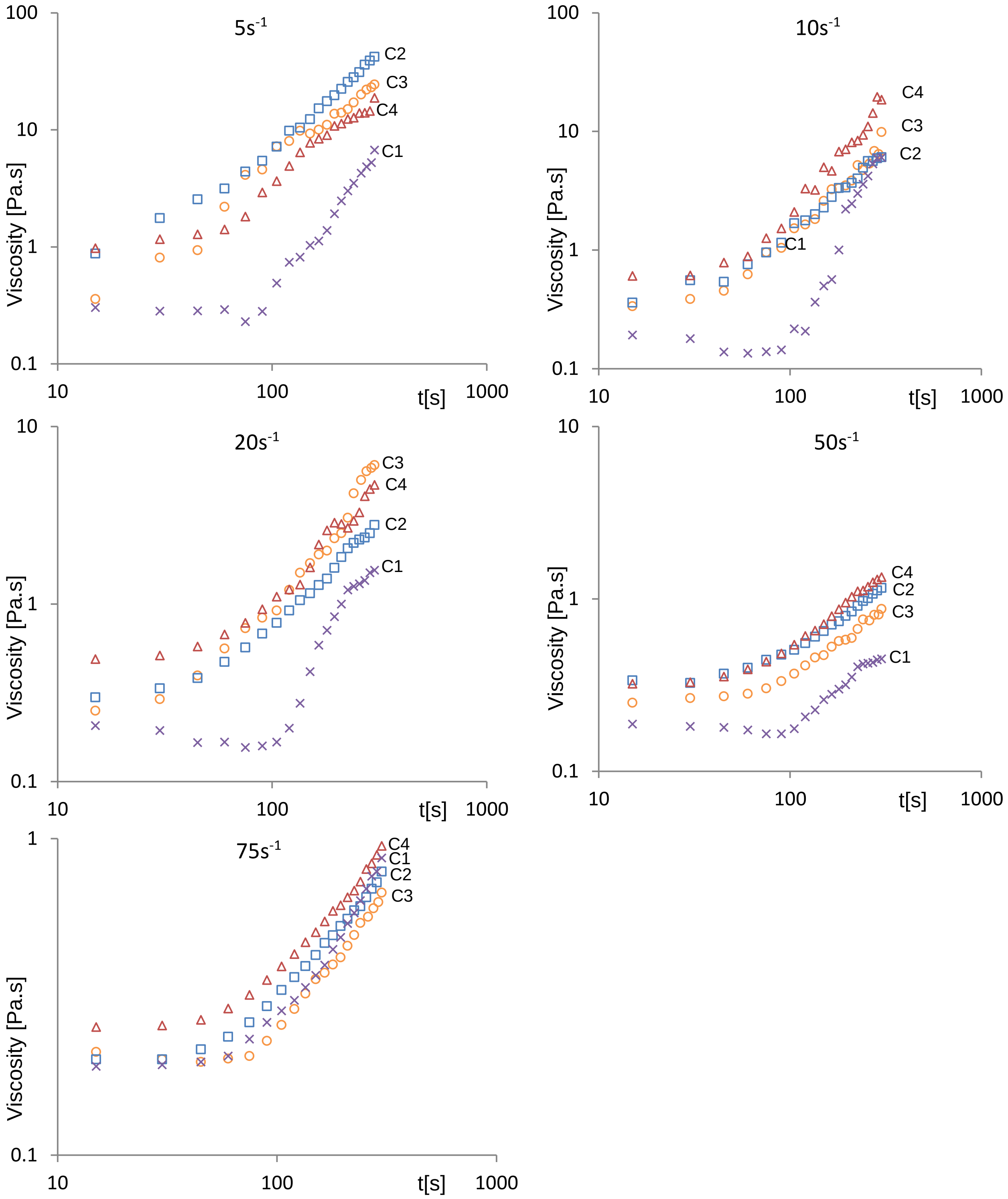


Figure 4.2: Evolution of viscosity over time at different constant shear rates of all cements with SP1 (0.3%)

The viscosity evolution of cement pastes with the addition of SP2 is depicted in Figure 4.3.

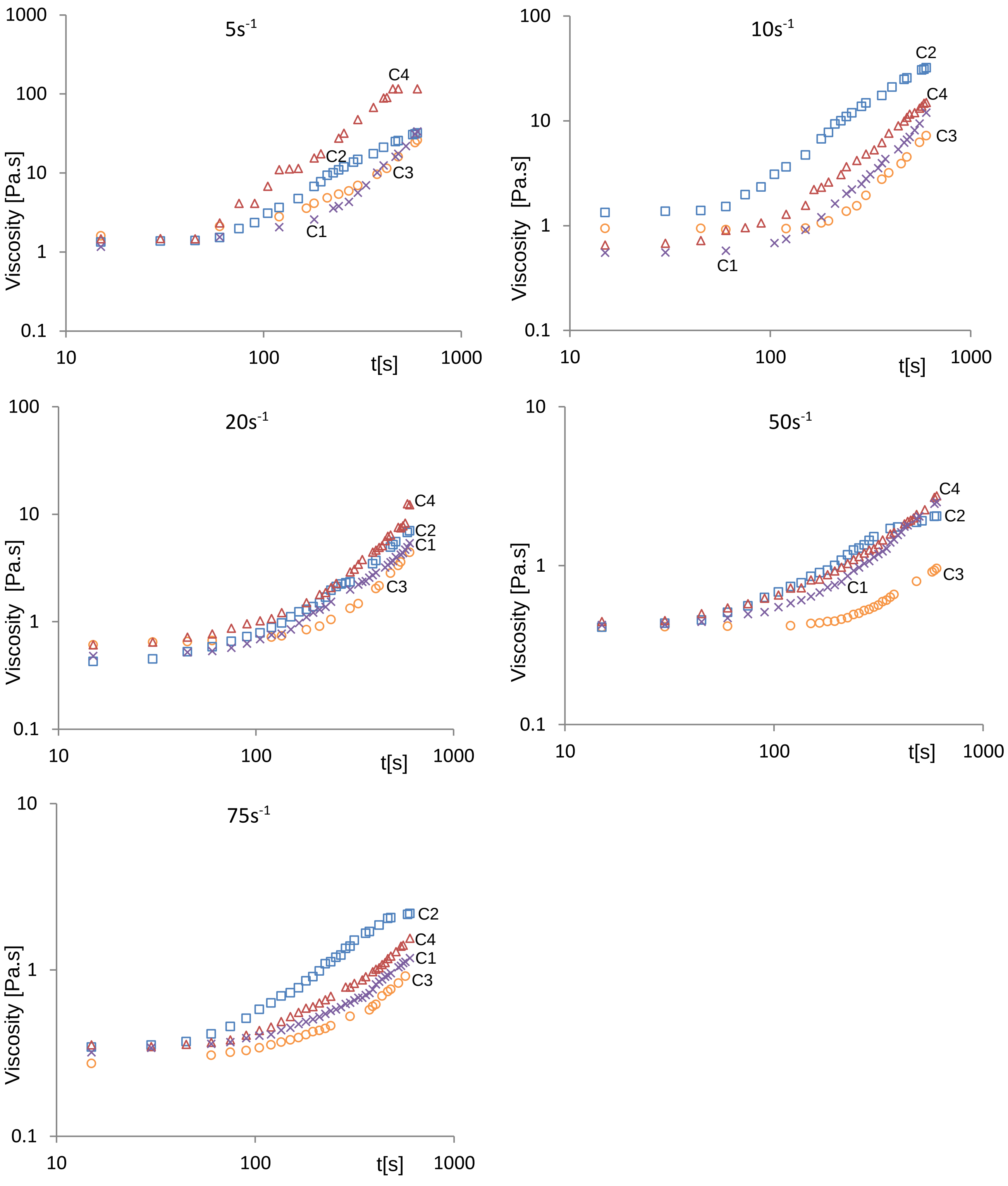
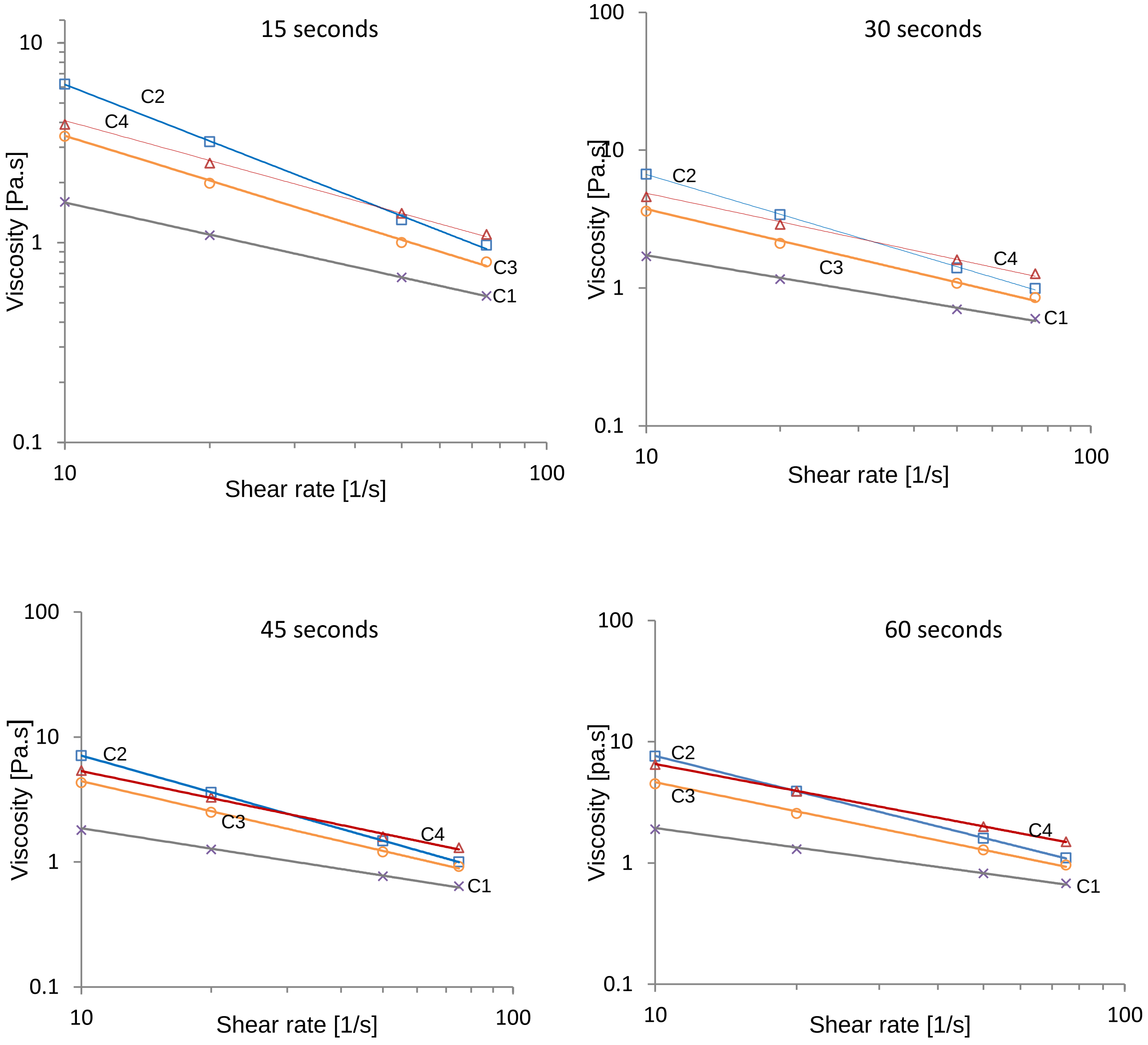


Figure 4.3: Evolution of viscosity in time at different constant shear rates of all cements with SP2 (0.3%)

In the presence of SP2, Cement C3 showed the lowest viscosity value at all the constant shear rates. There was a plateau at the beginning of the viscosity development, but the increase was not as sharp or sudden as for SP1 in Figure 4.2. With the addition of SP2, the plateau of the cements’ viscosity development seemed to be quite long as compared to that observed in Figure 4.2. At high constant shear rates, the viscosity values of all cements are almost the same for a few minutes after mixing time, increasing in different ways thereafter.

Viscosity curves

From the viscosity-time sweep curves, the viscosity-shear rate curves were deduced at different specific times of hydration. Figure 4.4 gives the viscosity-shear rate curves of all cements without the presence of SP in the corresponding pastes at different times of hydration.



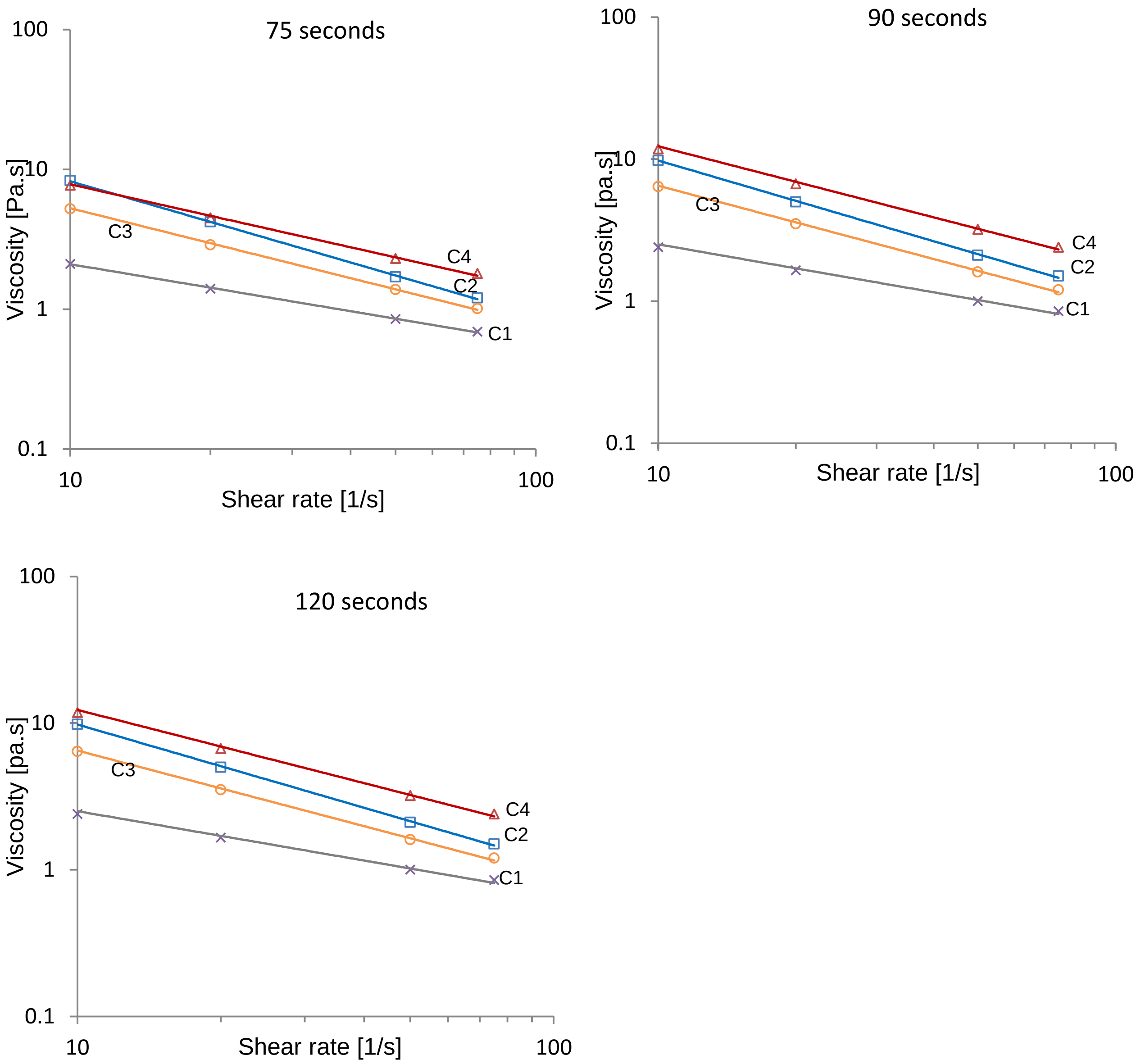
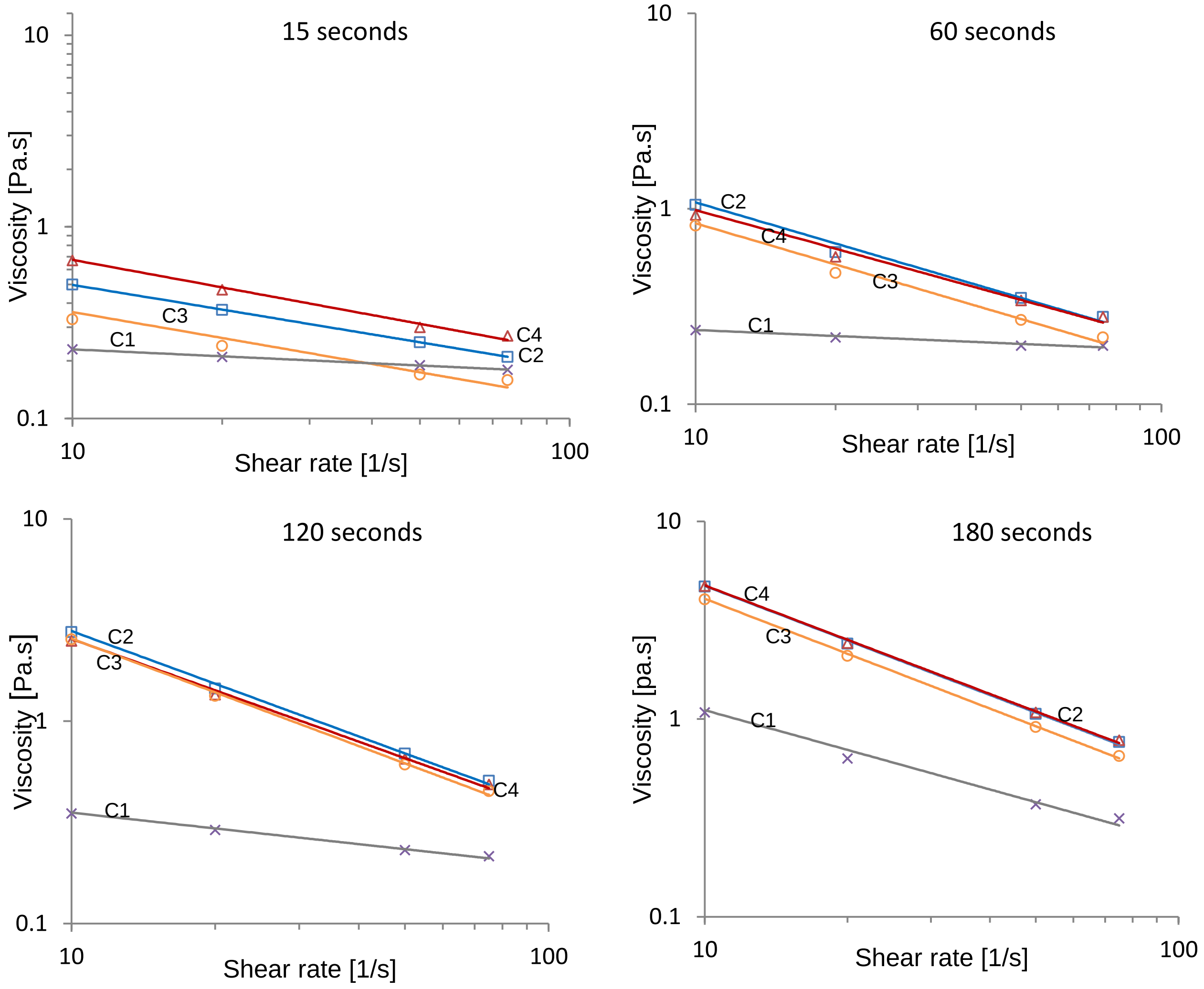


Figure 4.4: Viscosity curves at different times of all cements with no SP

These curves, constructed at different times, demonstrate that all cement pastes are shear thinning since the decrease in viscosity as the shear rate increases can be seen clearly. This is in agreement with the behaviour observed in the viscosity evolution, where the viscosity increased at each specific time. Cement C1 exhibited the lowest viscosity at all times compared to the other cements. The slope of each of curve seems to be parallel at each time, indicating the smooth increase in viscosity observed in Figure 4.1. The viscosity-shear rate curves of cements with SP1 at 0.3% at different times are shown in Figure 4.5.

It can be seen that the viscosity values of cements decreased with the addition of SP in the paste. Cement C1 seemed to be very sensitive to SP1 as it had the lowest viscosity values with a flat slope up to 60 seconds of hydration, corresponding to the plateau observed in the viscosity development in Figure 4.2. SP1 affects the other three cements, as seen the trends of the curves which are closely grouped. Shear thinning behaviour is also observed when using SP1 at optimum dosage (0.3%).



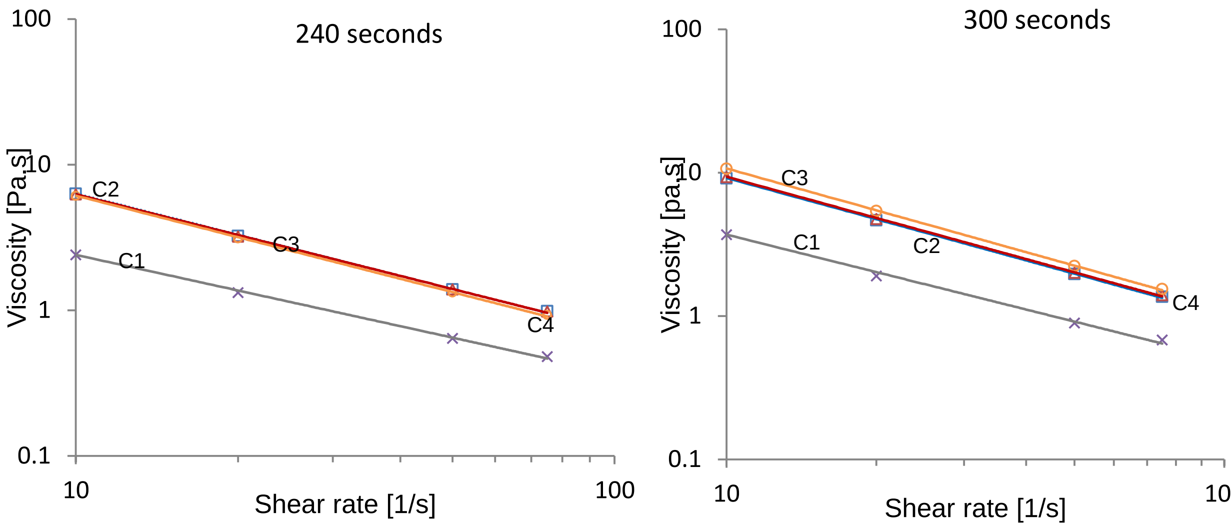
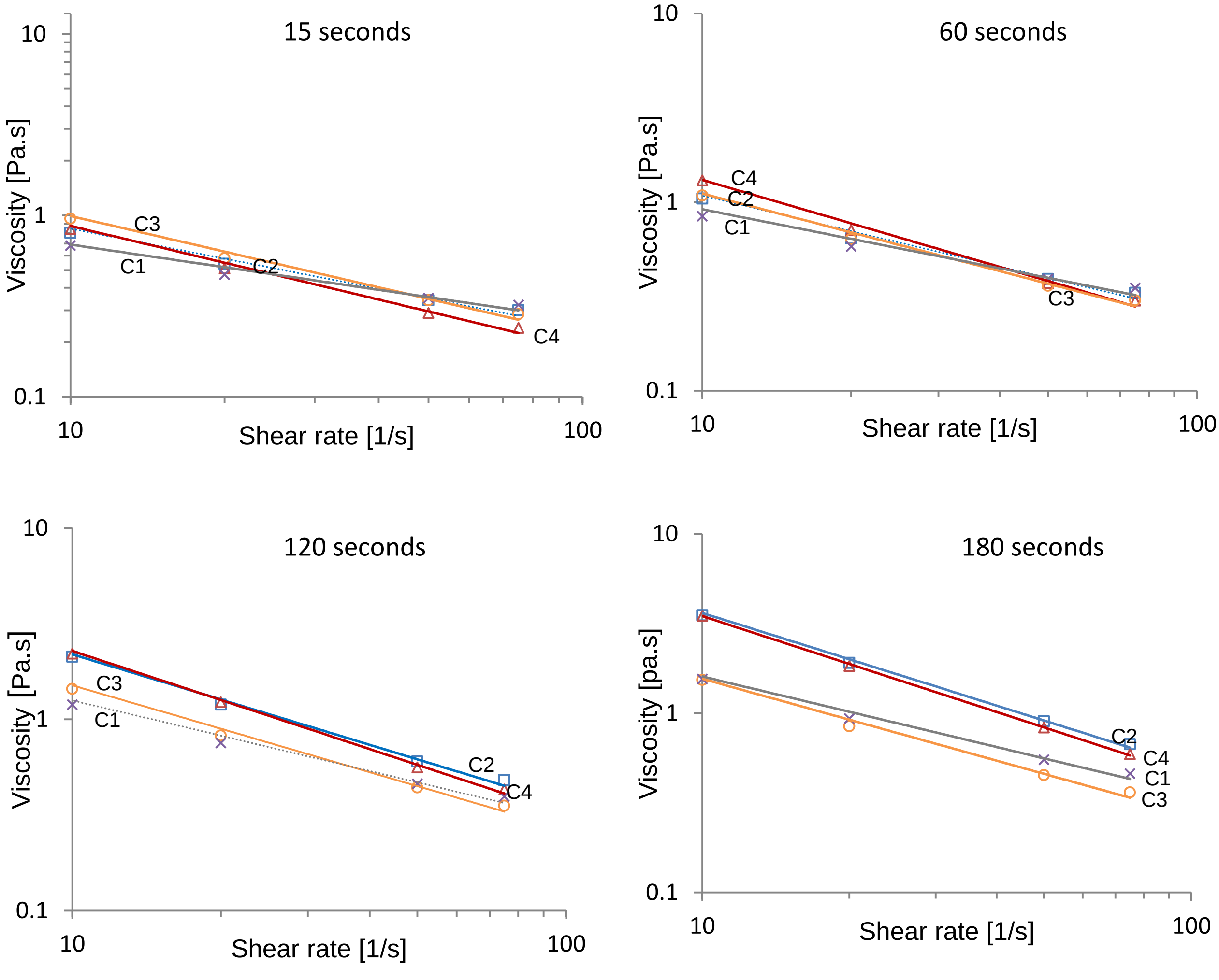


Figure 4.5: Viscosity curves at different time of all cements with SP1 (0.3%)

The viscosity-shear rate curves at different times of cements with SP2 at 0.3% is shown in Figure 4.6



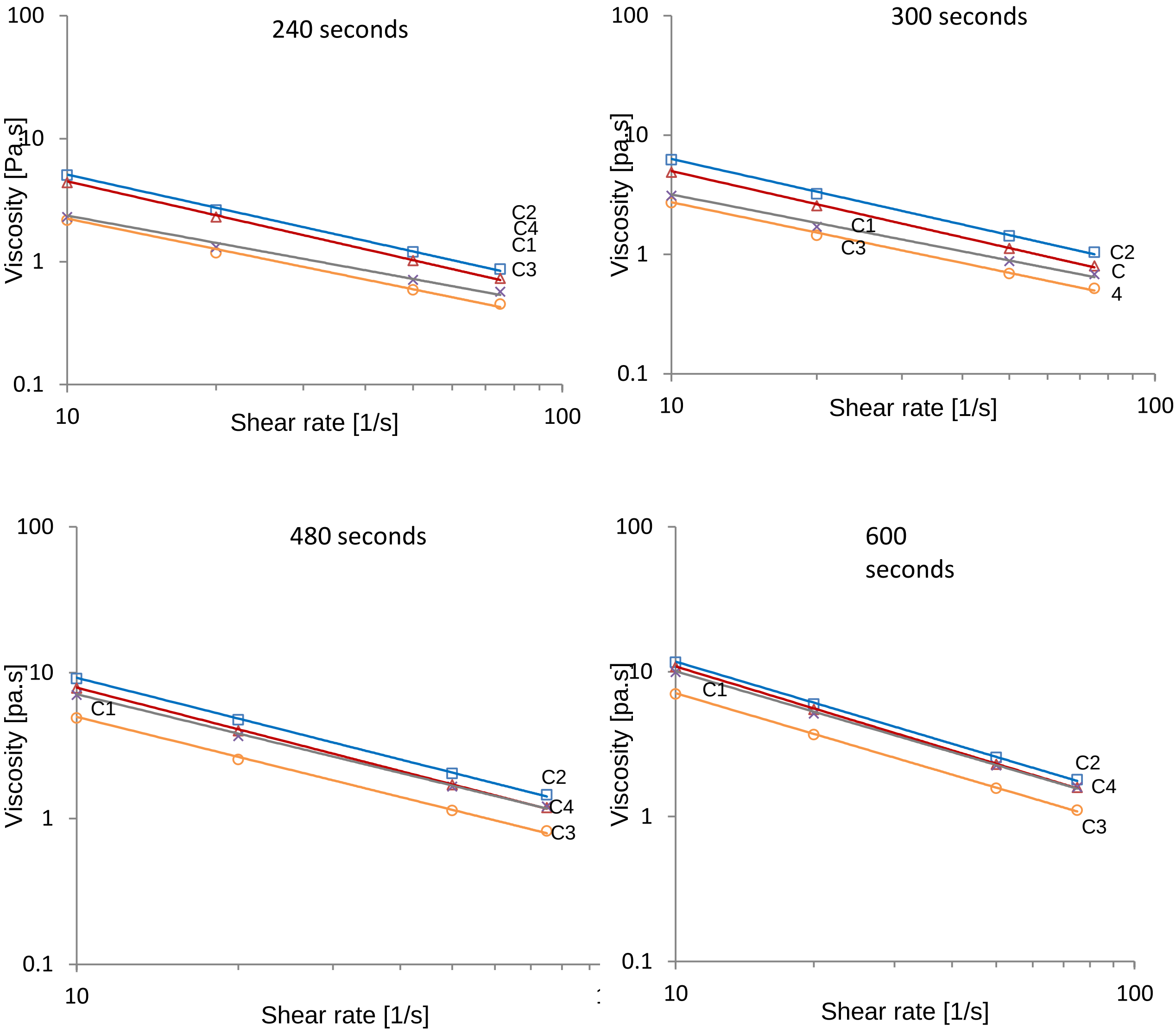
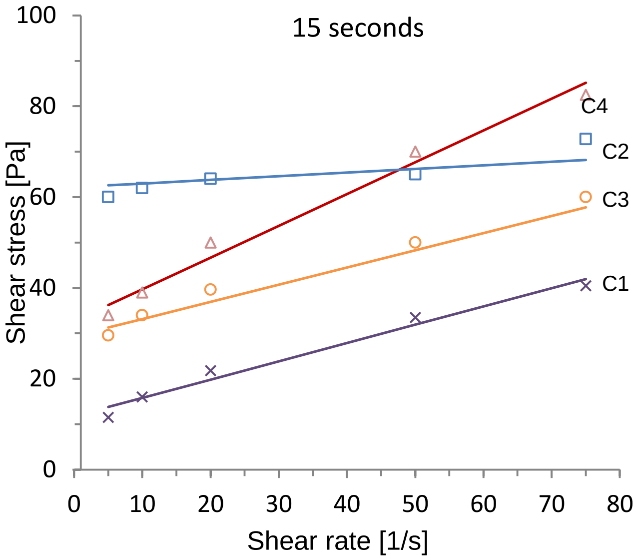


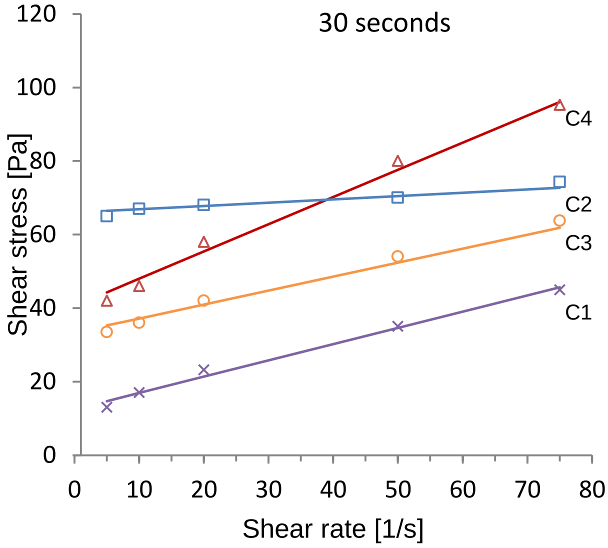
Figure 4.6: Viscosity curves at different time of all cements with SP2 (0.3%)

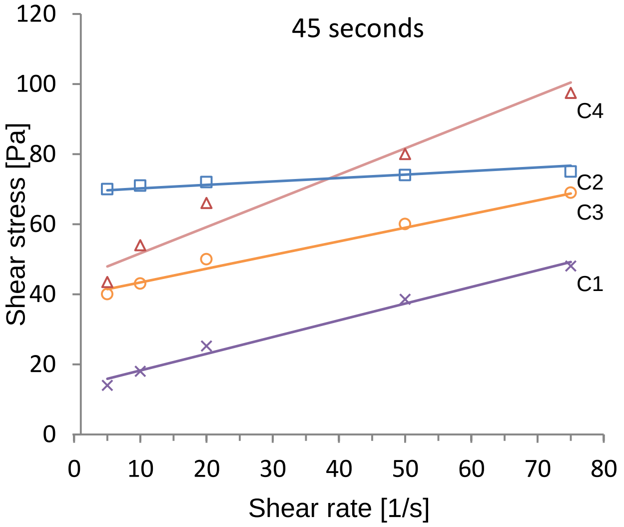
The effect of SP2 is similar for all cements, as can be seen by the slopes of the viscosity-shear rate curves. The values of viscosity, however, differ with Cement C2 having the highest and C3 the lowest. Shear thinning behaviour is observed with the addition of SP2.

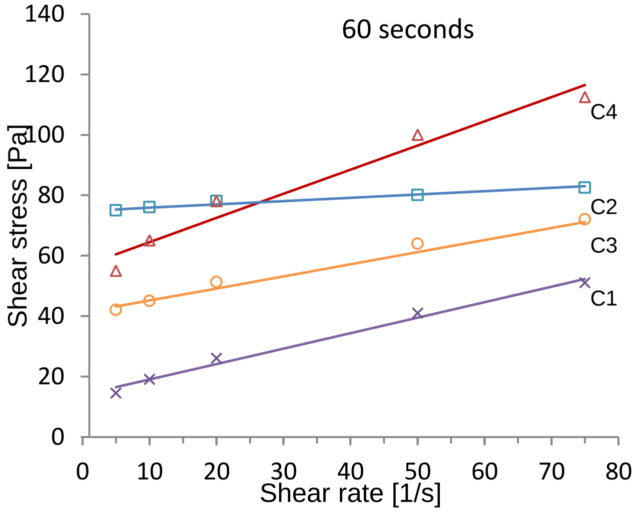
Flow curves

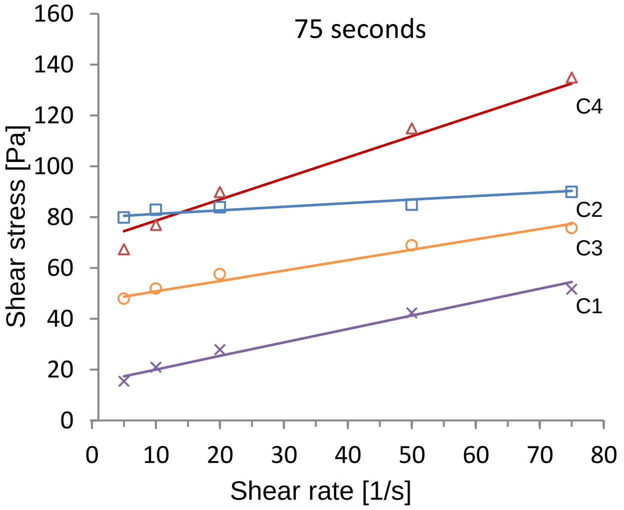
From the established viscosity curves at each time and for each shear rate, the corresponding shear stresses were established using the Bingham model and flow curves were constructed at a specific time. Figure 4.7 shows the flow curves of all cements without SP at different times:

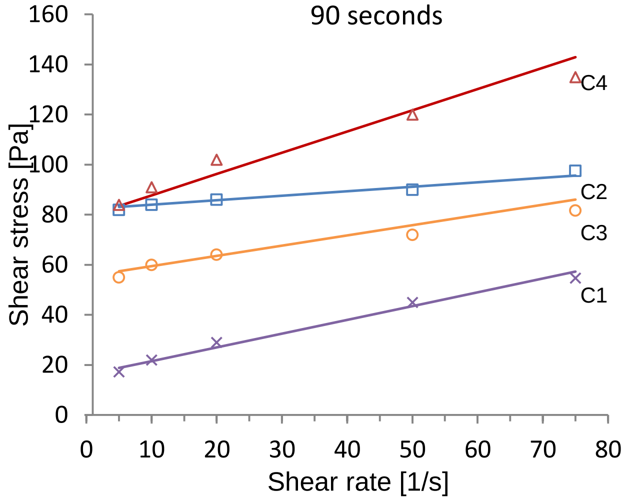

15 seconds
Shear stress [Pa]
0
20
40
60
80
100
Shear rate [1/s]
0
10
20
30
40
50
60
70
80
C4
C2
C3
C1


30 seconds
Shear stress [Pa]
0
20
40
60
80
100
120
Shear rate [1/s]
0
10
20
30
40
50
60
70
80
C4
C2
C3
C1


45 seconds
Shear stress [Pa]
0
20
40
60
80
100
120
Shear rate [1/s]
0
10
20
30
40
50
60
70
80
C4
C2
C3
C1


60 seconds
Shear stress [Pa]
0
20
40
60
80
100
120
140
Shear rate [1/s]
0
10
20
30
40
50
60
70
80
C4
C2
C3
C1


75 seconds
Shear stress [Pa]
0
20
40
60
80
100
120
140
160
Shear rate [1/s]
0
10
20
30
40
50
60
70
80
C4
C2
C3
C1


90 seconds
Shear stress [Pa]
0
20
40
60
80
100
120
140
160
Shear rate [1/s]
0
10
20
30
40
50
60
70
80
C4
C2
C3
C1

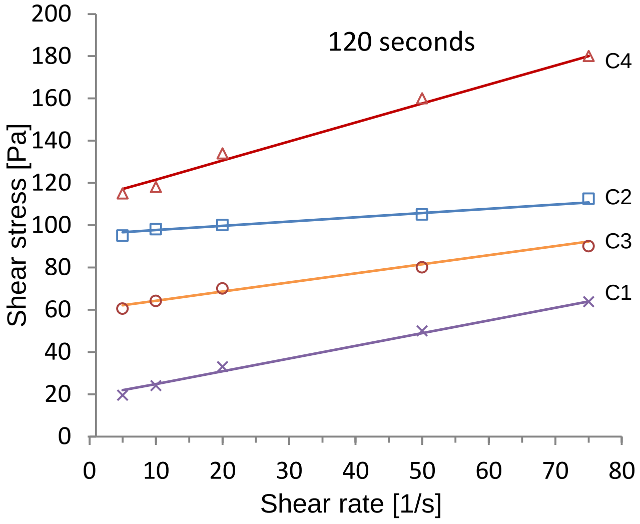


Figure 4.7: Flow curves at different times fitted by Herschel Bulkley model for all cements with no SP

The flow behaviours of all cement pastes in the absence of SP are well predicted by the Hershel Bulkley model, with a yield stress value that evolves as the hydration time increases. However, Cement C1 had the lowest yield stress values as compared to the rest of the cements at all considered times. The Bingham viscosity of all cements seems to be constant at all times and Cements C4 and C2 have, respectively, the highest and lowest values as compared to the rest of cements. The change of rheological parameters over time for the four cements is shown in Table 4.1.

Table 4.1: Coefficients values of Bingham model $\boldsymbol{\tau} = \boldsymbol{\tau_y} + \boldsymbol{k}\dot{\boldsymbol{\gamma}}$ of cements with no SP

Time (s)	**C1**		**C2**		**C3**		**C4**	
	τ_y **[Pa]**	k	τ_y **[Pa]**	k	τ_y **[Pa]**	k	τ_y **[Pa]**	k
15	**12**	**0.4**	**62**	**0.1**	**29**	**0.4**	**33**	**0.7**
30	**12**	**0.4**	**66**	**0.1**	**33**	**0.4**	**41**	**0.7**
45	**14**	**0.5**	**69**	**0.1**	**40**	**0.4**	**44**	**0.8**
60	**14**	**0.5**	**75**	**0.1**	**41**	**0.4**	**56**	**0.8**
75	**15**	**0.5**	**80**	**0.1**	**47**	**0.4**	**70**	**0.8**
90	**16**	**0.6**	**85**	**0.2**	**55**	**0.4**	**79**	**0.9**
120	**19**	**0.6**	**96**	**0.2**	**60**	**0.4**	**113**	**0.9**

This table clearly reveals the evolution of both yield stress and plastic viscosity for each cement. Cement C1 has the lowest values of yield stress and changes slowly over time. Cement C4 has the highest yield stress values and changes significantly over time. The plastic viscosity values, however, are reasonably constant for all cements. The evolution of rheological parameters (yield stress and plastic viscosity) is illustrated in Figure 4.8 and Figure 4.9.

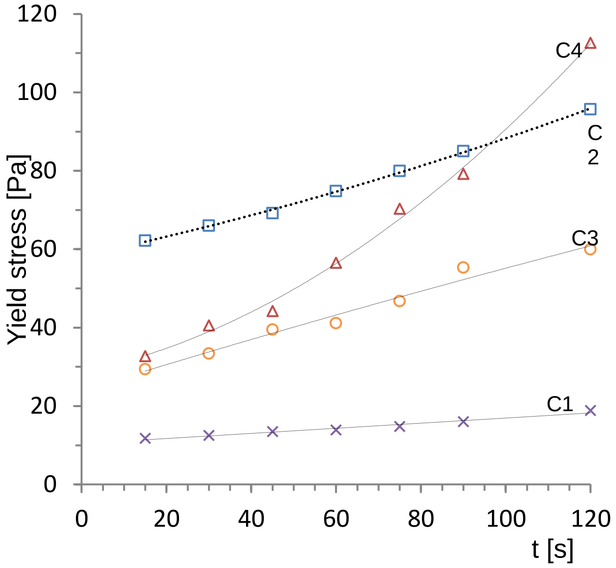


Figure 4.8: Yield stress evolution of cement without SP

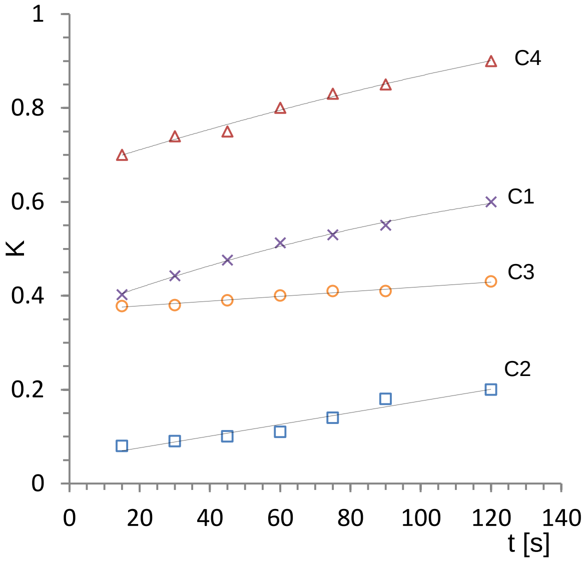


Figure 4.9 Plastic viscosity evolution of cements without SP

From Figure 4.8, it is evident that Cement C1 exhibited a slow yield stress development with an almost horizontal slope, while Cement C4 presented a sharp slope demonstrating a fast yield stress development. Cement C2 had great yield stress values compared to Cement C3, but with the same slope. Concerning the change in plastic viscosity, Figure 4.9 shows that Cement C4 presented the highest values, followed by Cement C1 which had the same slope. Cement C2 exhibited the lowest values with a slope almost identical to C4 and C1. The effect of SP1 on the rheological parameters for each cement is presented in Table 4.2 and in Figure 4.10 and Figure 4.11. The corresponding flow curves can be found in Appendix B.

Table 4.2: Yield stress and viscosity values over time of cements with SP1 (0.3%)

Time (s)	**C1**		**C2**		**C3**		**C4**	
	τ_y [Pa]	**k**	**τ_y [Pa]**	**k**	**τ_y [Pa]**	**k**	**τ_y [Pa]**	**k**
15	**0.6**	**0.2**	**3**	**0.2**	**2**	**0.1**	**6**	**0.2**
60	**0.4**	**0.2**	**9**	**0.2**	**7**	**0.1**	**9**	**0.2**
120	**1.5**	**0.2**	**26**	**0.2**	**24**	**0.1**	**23**	**0.2**
180	**8.5**	**0.2**	**45**	**0.2**	**39**	**0.1**	**45**	**0.2**
240	**21.6**	**0.2**	**61**	**0.2**	**59**	**0.1**	**60**	**0.2**
300	**35.0**	**0.2**	**85**	**0.2**	**105**	**0.1**	**91**	**0.2**

When introducing SP1 in cements, both yield stress and plastic viscosity values decreased. The initial yield stress values were reduced to just few Pascal and the viscosity values were reduced by about 75%. Cement C1 had the lowest yield stress values, increasing less than the others over time. The yield stress of other cements was similar. The plastic viscosity values remained constant over time for all cements and were similar, the exception being Cement C3 that had the lowest values.

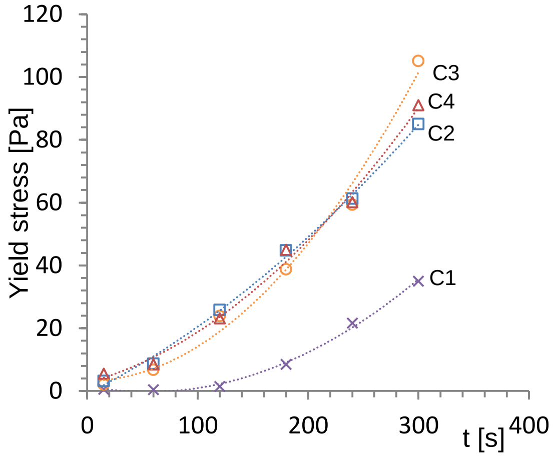


Figure 4.10: Yield stress evolution of cement with SP1 (0.3%)

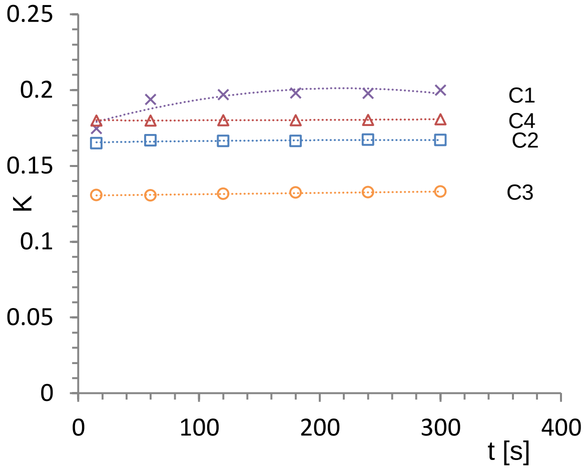


Figure 4.11: Plastic viscosity evolution of cements with SP1 (0.3%)

The yield stress development of all cements in the presence of SP1 is depicted in Figure 4.10. Cements C2, C3 and C4 seemed to be affected in the same way. Cement C3 showed the largest increase in yield stress, followed by Cements C2 and C4, and then Cement C1.

The effect of SP2 on the yield stress and plastic viscosity for all cements is shown in Table 4.3, their rheological behaviour trends in Figure 4.12 and Figure 4.13

Table 4.3: Yield stress and viscosity values over time of cements with SP2 (0.3%)

Time (s)	C1		C2		C3		C4	
	τ_y [Pa]	k	τ_y [Pa]	k	τ_y [Pa]	k	τ_y [Pa]	k
15	4	0.3	6	0.2	8	0.2	7	0.1
60	6	0.3	8	0.2	9	0.2	11	0.1
120	9	0.3	19	0.2	13	0.2	21	0.2
180	12	0.3	33	0.2	13	0.2	33	0.2
240	20	0.3	48	0.2	20	0.2	43	0.2
300	28	0.3	60	0.2	25	0.2	48	0.2
480	67	0.3	89	0.3	47	0.2	77	0.2
600	96	0.3	114	0.3	68	0.2	106	0.2

It can be seen that with SP2, the yield stress, as well as plastic viscosity values, decreased significantly compared to where there was no SP in the paste, as per Table 4.1. The yield stress evolution of all cements in Figure 4.12 showed that Cements C1 and C3 began with small yield stress values, before increasing significantly. However, these values could not be greater than those of Cement C2 and C4. The plastic viscosity values in Figure 4.13 decreased as well, and there is not much change observed over time. Cement C1 seemed to have the highest values, followed by Cements C2, C3 and C4.

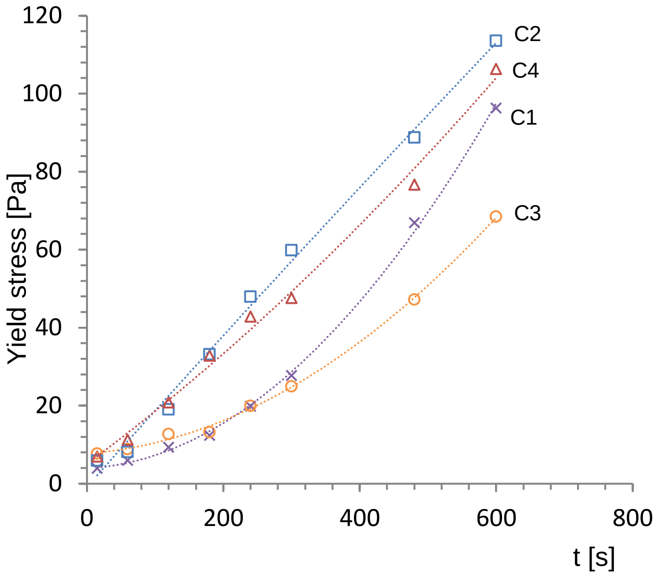


Figure 4.12: Yield stress evolution of cement with SP2 (0.3%)

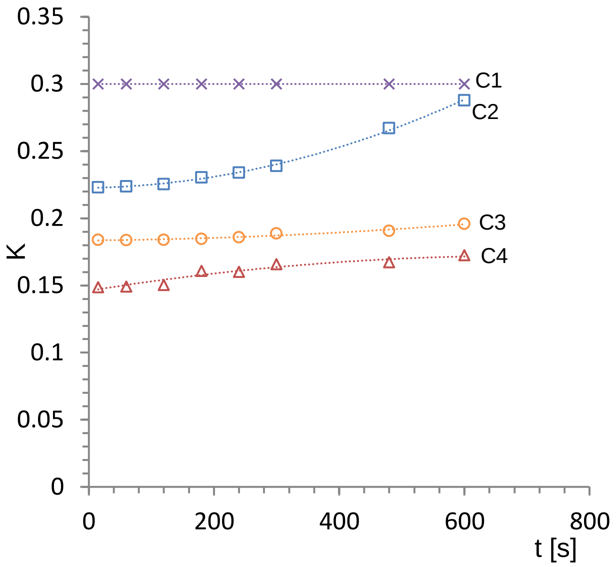


Figure 4.13: Plastic viscosity evolution of cements with SP2 (0.3%)

4.1.2 Determination of yield stress and plastic viscosity from hysteresis loops

This method has been used by many researchers to determine both the yield stress and viscosity values of cement paste. As described in section 2.3.7, this method consists of determining the yield stress and the viscosity values from the downward branch of the hysteresis loop by extrapolation of the experimental data to zero shear rates. The extrapolation procedure is performed by linear dependence of the shear stress on shear rate (i.e. with the Bingham equation).

All hysteresis loops presented the expected shapes, as explained by Banfill and Saunders (1981). The cycle time was short and therefore the hydration time was reduced. Consequently, the structure build up was slow compared to the rate of breakdown, causing the down curve to fall below the up curve. Figure 4.14 shows the rheological parameters of Cement C1 without SP.

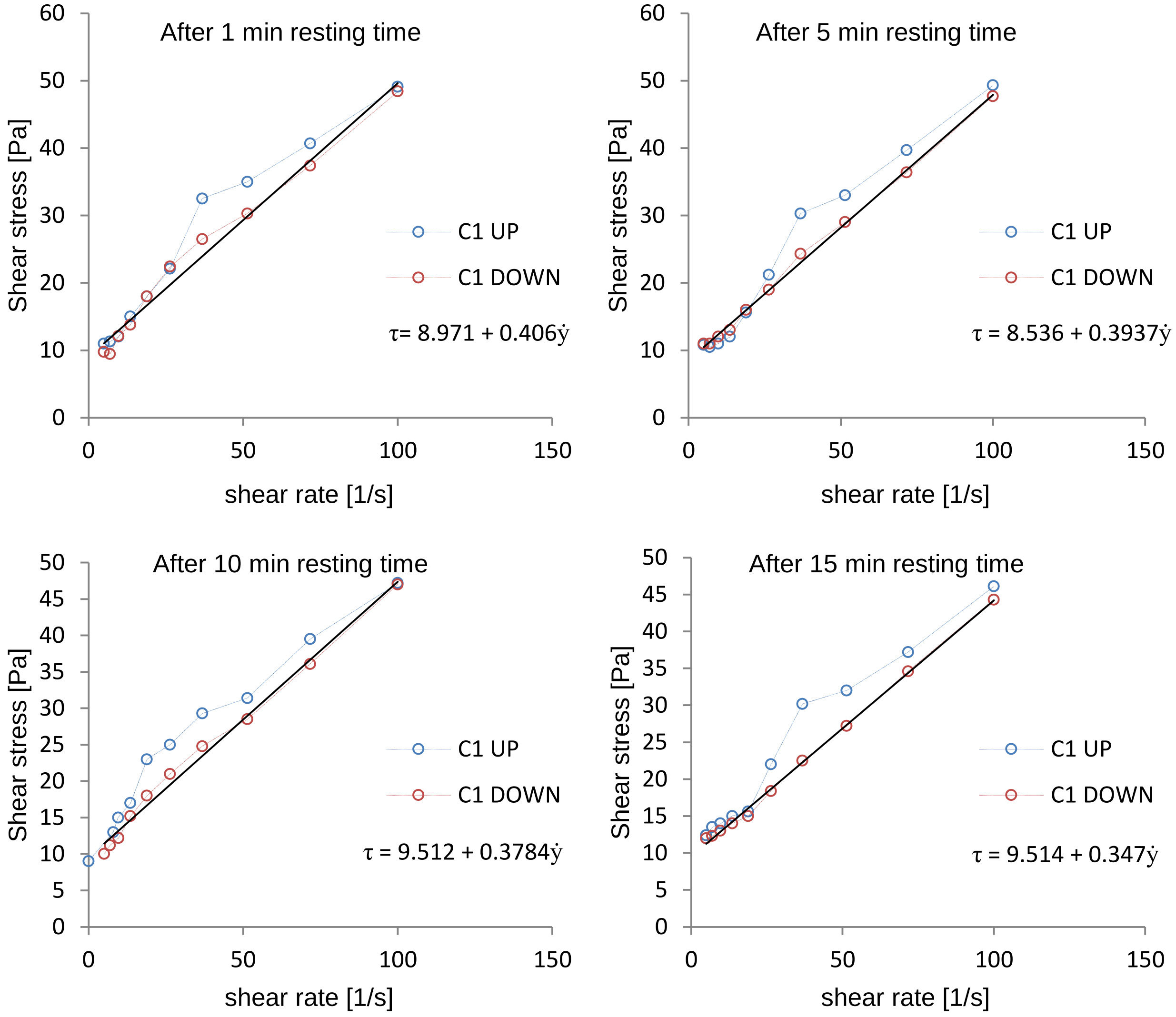


Figure 4.14: Rheological parameters from hysteresis loop after different times for Cement C1 with no SP

After one minute of resting time, the yield stress value is about 9 Pa. The value did not change significantly, as up to 15 minutes it was approximately 9.5 Pa. The plastic viscosity values are constant for all the resting times and were about 0.4 Pas. Appendix C gives the hysteresis loops of all other three cements without SP.

The values of yield stress (20 Pa) of Cement C2 remained constant during the first 10 minutes of resting time, before it suddenly increased to 27 Pa after 15 minutes of resting time. The plastic viscosity values remained constant at about 0.4 Pas.

In the absence of SP, the values of yield stress for Cement C3 did not change significantly.

These values varied only from 20 to 23 Pa respectively from one to 15 minutes of resting time, while the plastic viscosity values changed slightly from 0.4 to 0.5 Pas.

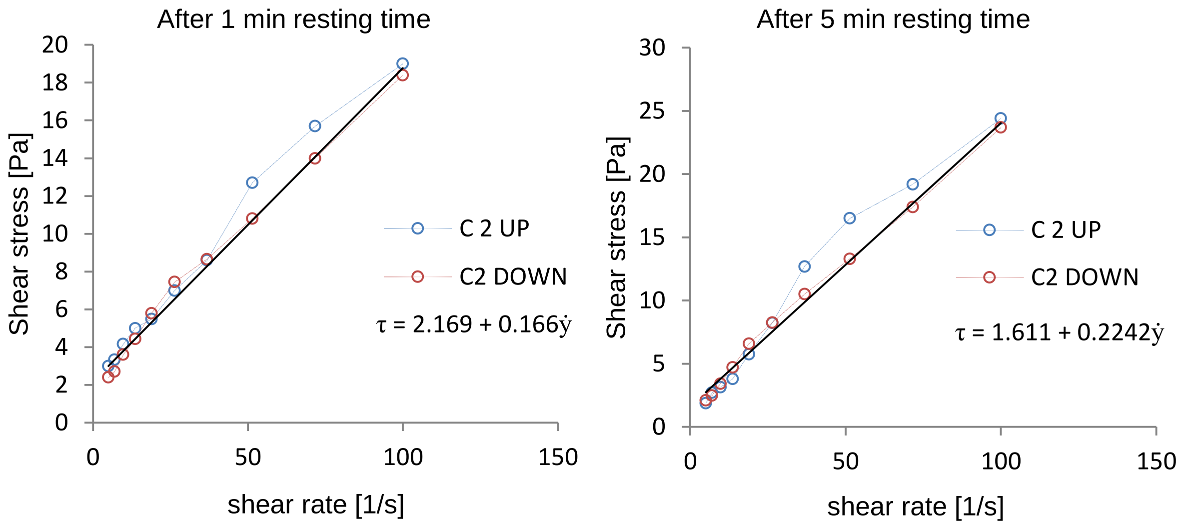
Cement C4 with no SP in the paste showed few changes in its rheological parameters. The yield stress increased from 26 Pa to 36 Pa and the plastic viscosity values from 0.4 to 0.5 Pas.

Table 4.4 summarises all the yield stress values of all cements without SP, according to their corresponding resting time.

Table 4.4: Yield stress values determined by hysteresis loop for all cements without SP

	Yield stress vslues [Pa] for cements with no SP			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**9**	**20**	**20**	**25**
5	**9**	**20**	**20**	**25**
10	**10**	**20**	**23**	**32**
15	**10**	**27**	**23**	**33**

Typical example of hysteresis loops when SPs were added in the cement paste are given in the following figures. Figure 4.15 depicts the interaction of SP1 with C2 regarding its rheological parameters and for other cements, the corresponding figures can be found in Appendix D.



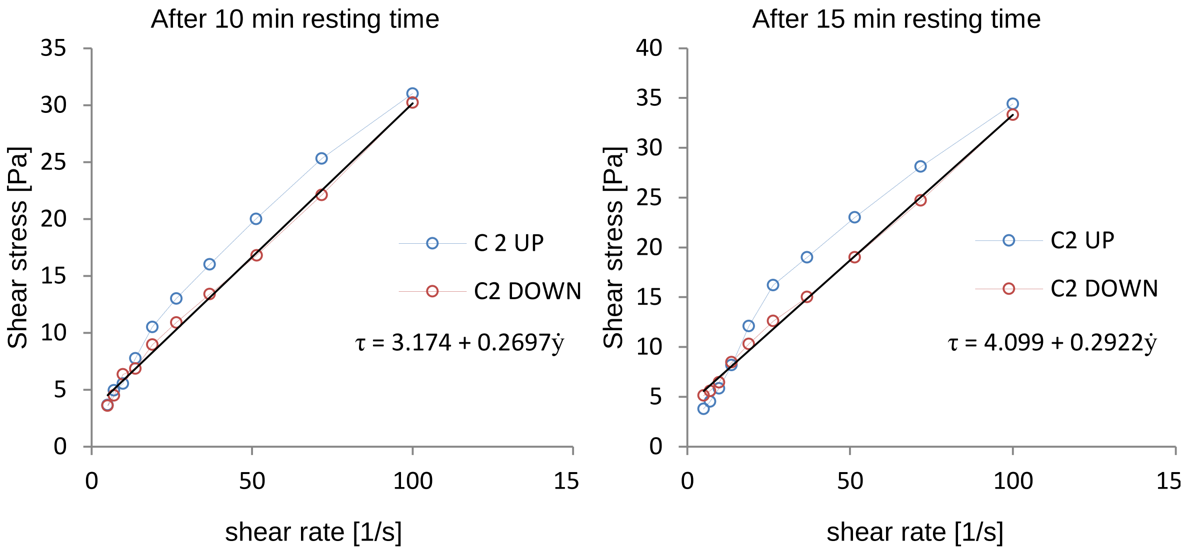


Figure 4.15: Rheological parameters from hysteresis loop after different times for Cement C2 with SP1 (0.3%)

It is evident that SP1 decreased significantly the values of yield stresses, and the plastic viscosity values changed slightly over time. After one minute of resting time, the yield stress value was approximately 2 Pa, while 15 minutes later the yield stress recorded was approximately 4 Pas. The plastic viscosity was constant 0.2 Pa.s up to 10 minutes and increased to 0.3 thereafter.

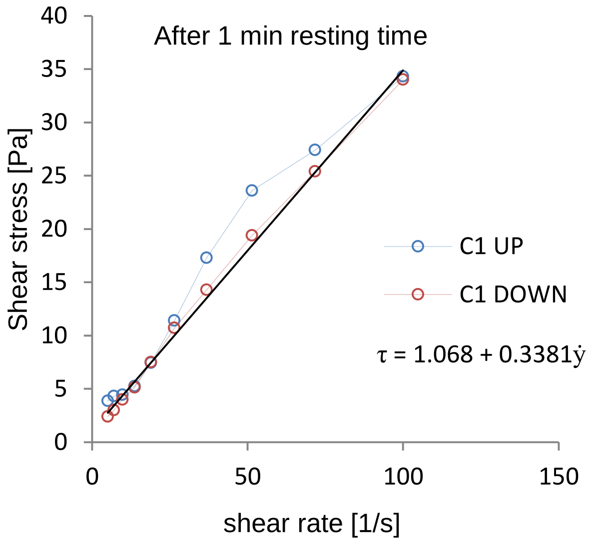
The yield stress values of Cement C3 with SP1 are significantly decreased in the order of 10^{-1} Pa and did not change over time. The value went from 0.1 to 0.2 Pa while the plastic viscosity values started from 0.2 to 0.3 Pa.s after 15 minutes of resting time.

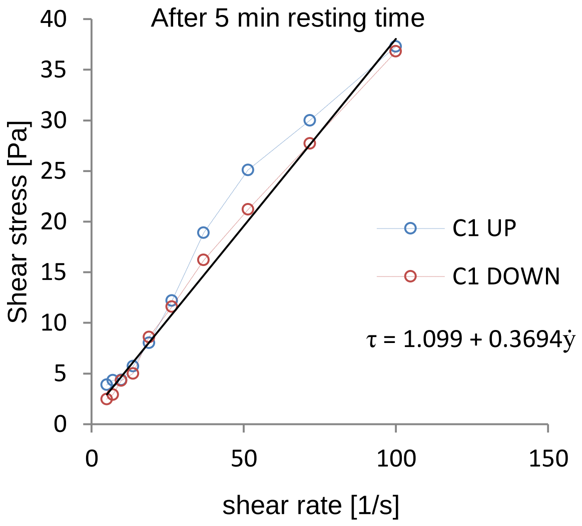
Cement C4 showed the highest values of yield stress as compared to the other cements in the presence of SP1. However, compared to the instance when there was no SP in the paste, these values seemed to be decrease significantly. The values appeared to be constant as the resting time evolved. The plastic viscosity was about 0.3 Pas and the yield stress 13 Pa. Yields stress values for each cement with SP1 at each resting time are summarised in Table 4.5.

Table 4.5: Yield stress values determined by hysteresis loop for all cements with SP1

	YIELD STRESS VALUES[Pa] CEMENT WITH SP1			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**0**	**2**	**0.1**	**11**
5	**0**	**2**	**0.1**	**13**
10	**0**	**3**	**0.2**	**13**
15	**0**	**4**	**0.2**	**14**

The interaction of cements with SP2 in terms of their rheological parameters was as follows. The hysteresis loops of Cement C1 with SP2 are presented in Figure 4.16 and the three other cements are shown in Appendix E.





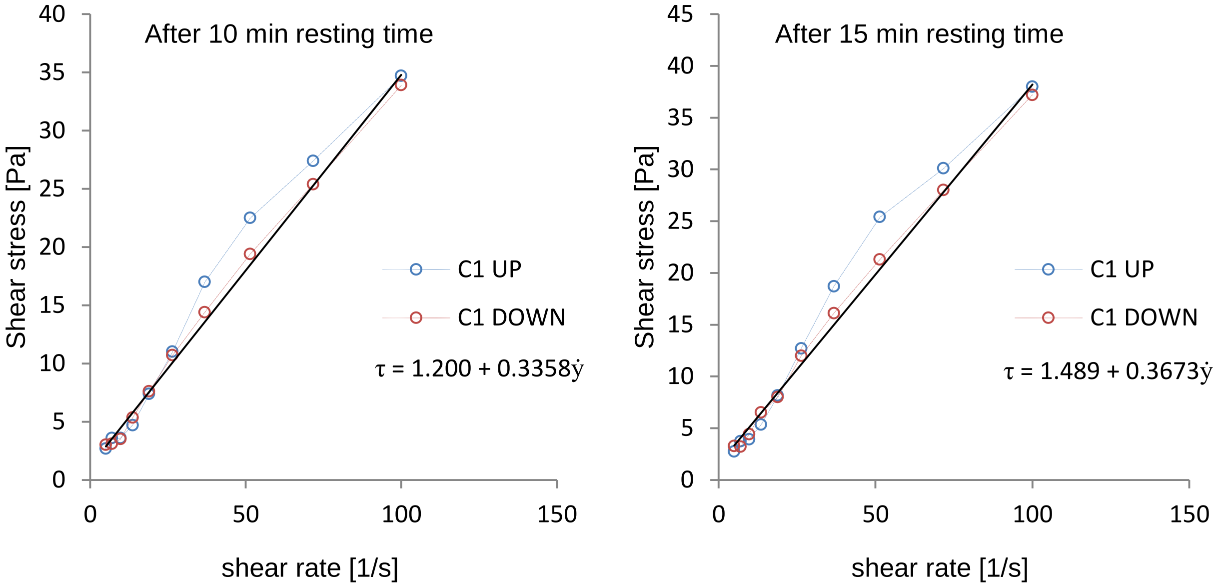


Figure 4.16: Rheological parameters from hysteresis loop after different times for Cement C1 with SP2 (0.3%)

The yield stress value of Cement C1 decreased with the addition of SP2 in the paste to about 1 Pa, and its initial plastic viscosity was about 0.4 Pas, remaining constant at all the different resting times.

The introduction of SP2 in Cement C2 decreased its yield stress value to around 3 Pa after one and five minutes of resting time, slightly increasing up to 5 Pa after 10 and 15 minutes of resting time. The plastic viscosity values changed from 0.3 to 0.4 respectively after one and 15 minutes of resting time.

In the presence of SP2, Cement C3 exhibited Newtonian behaviour from one to 10 minutes of resting time. The yield stress values slightly increased up to 0.2 Pa only after 15 minutes of resting time. The plastic viscosity values were constant during all the resting times and were estimated at 0.3 Pas

The yield stress values at different resting times of Cement C4 in the presence of SP2 did not show significant change. At one minute of resting time, the yield stress was about 5 Pa; at five minutes, it changed to 6 Pa; and thereafter 8 Pa. The plastic viscosity remained constant throughout different resting times and was estimated at 0.4 Pas. The yield stress values of all cements with SP2 are summarised in Table 4.6.

Table 4.6: Yield stress values determined from hysteresis loops for all cements with SP2

	YIELD STRESS VALUES[Pa] CEMENT WITH SP2			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**1**	**3**	**0**	**5**
5	**1**	**3**	**0**	**6**
10	**1**	**5**	**0**	**8**
15	**1**	**5**	**0.2**	**8**

4.2 Elastic properties

4.2.1 Determination of yield stress value from amplitude sweep

This method consists of calculating the yield stress value of cement paste from the amplitude sweep versus storage modulus curve, as explained in section 3.3. The yield stress value is calculated from the shear strain value where the storage modulus G’ starts dropping or deviating from the horizontal slope, the region where cement particles are very close to each other causing cement paste to behave as a solid material (Schultz & Struble, 1992).

Figure 4.17 presents the storage modulus versus strain sweep of all cements without SP

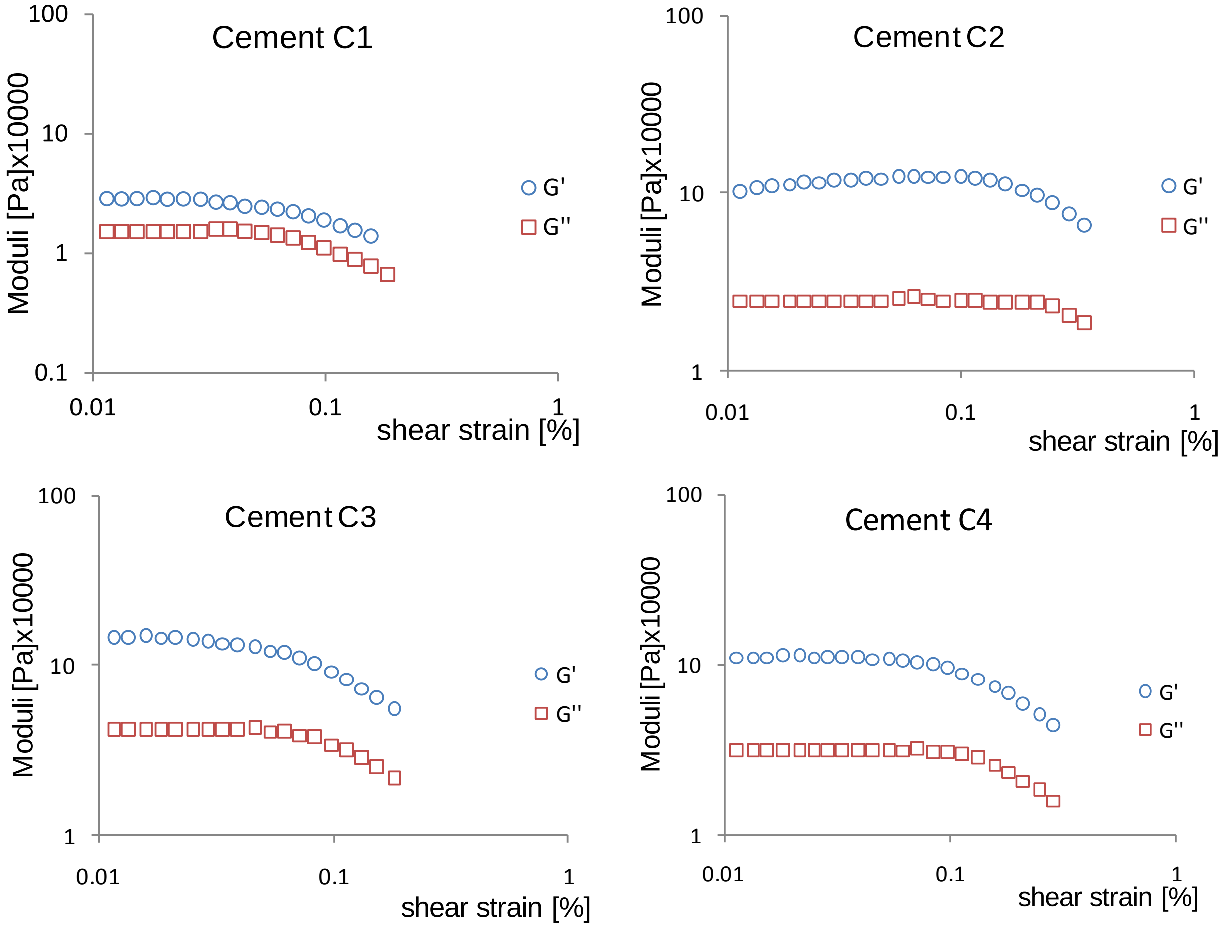


Figure 4.17: Storage modulus against amplitude sweep for all cements without SP

The corresponding yield stress values for each cement without SPs are as tabulated in Table 4.7. There is a significant difference between the lowest and the highest yield stress values (19-117 Pa).

Table 4.7: Yield stress values determined by amplitude sweep of all cements without SP

	CEMENT WITHOUT SP			
	C1	**C2**	**C3**	**C4**
Yield stress [Pa]	**19**	**102**	**68**	**117**

Figure 4.18 shows the dependency of storage modulus on strain sweep for all cements in the presence of SP1.

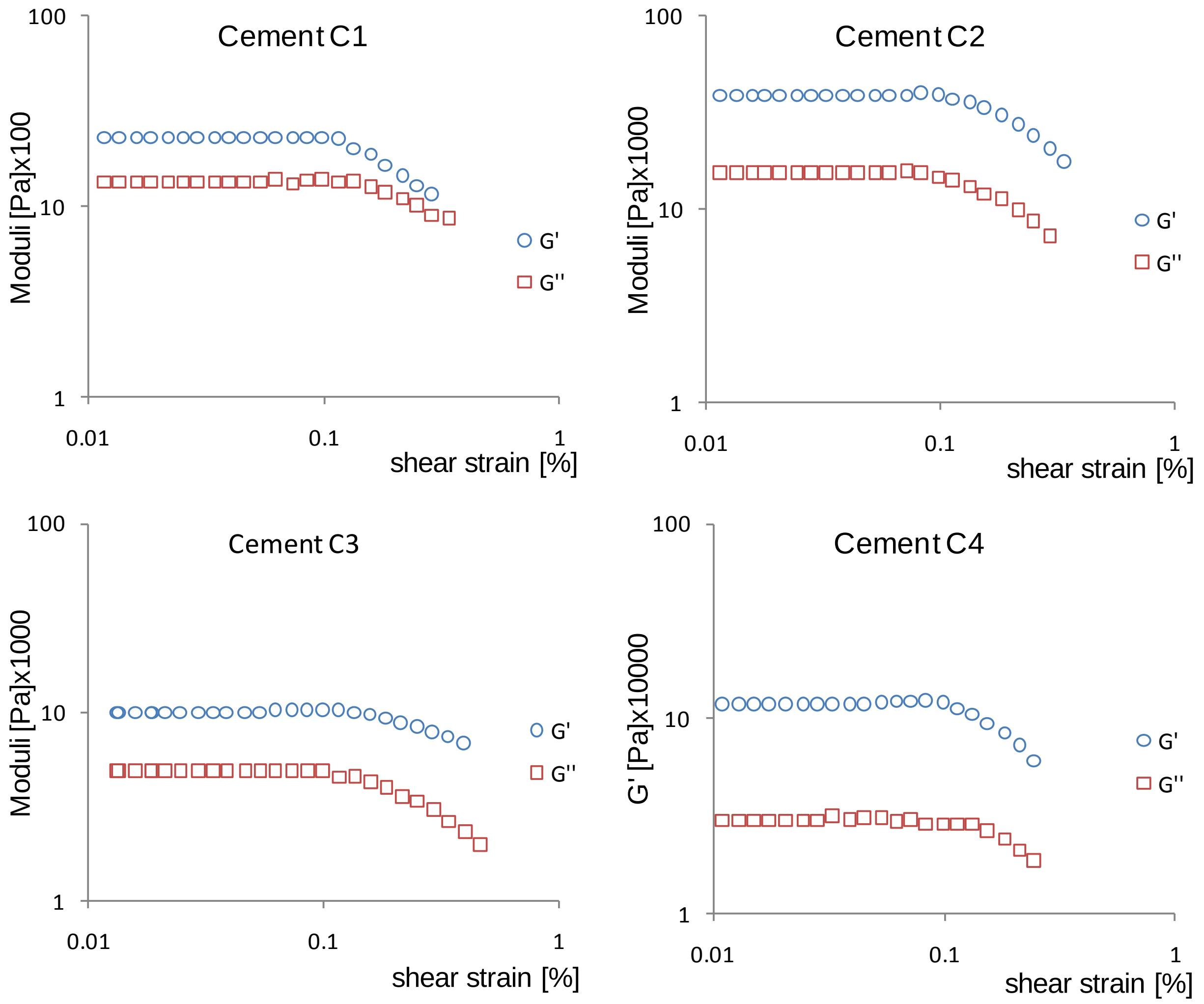


Figure 4.18: Storage modulus against amplitude sweep for all cements with SP1 (0.3%)

The values of yield stress for each cement when SP1 was incorporated in the paste are presented in Table 4.8.

Table 4.8: Yield stress values determined by amplitude sweep of all cements with SP1 (0.3%)

	YIELD STRESS [Pa] OF CEMENTS WITH SP1 [Pa]			
	C1	**C2**	**C3**	**C4**
Yield stress [Pa]	**4**	**50**	**23**	**100**

The effect of SP1 is more pronounced on Cements C1 and C3 where the yield stress values are significantly decreased. Cements C2 and C4 had the highest yield stress values. However, Cement C4 had a value two times more than C2 yield stress value. The highest yield stress value (C4) was twenty times more the lowest yield stress value (C1).

The effect of SP2 on all cements is illustrated in Figure 4.19, and respective yield stress values are in Table 4.9.

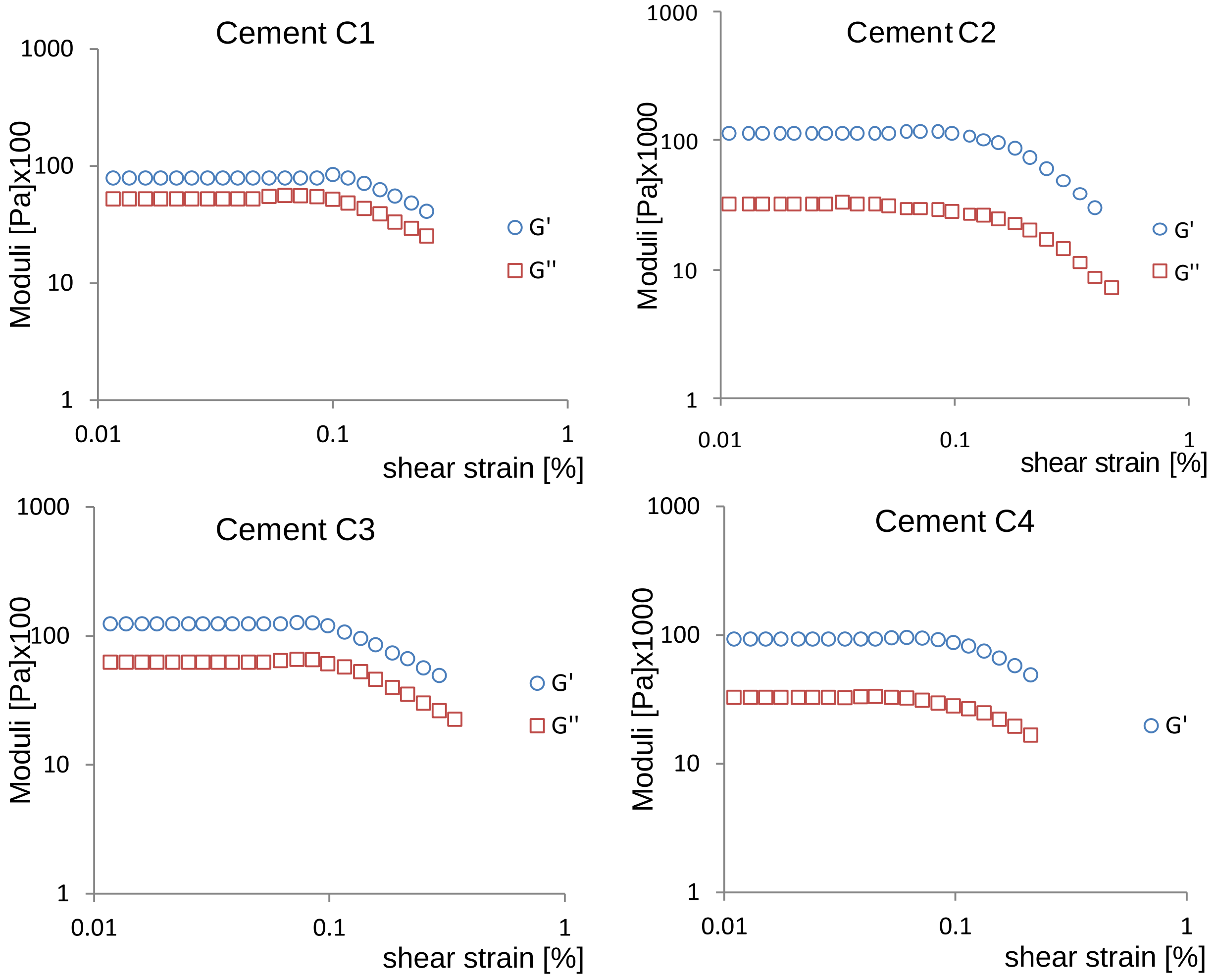


Figure 4.19: Storage modulus against amplitude sweep for all cements with SP2 (0.3%)

Table 4.9: Yield stress values determined by amplitude sweep for all cements with SP2 (0.3%)

	CEMENT WITH SP2 [Pa]			
	C1	**C2**	**C3**	**C4**
Yield stress [Pa]	**10**	**73**	**14**	**53**

Cements C1 and C3 experienced the lowest yield stress values while Cement C2 presented the highest yield stress value and was also about two times more than Cement C4 values. The difference between the highest (C2) and the lowest (C1) yield stress value was six times more than the lowest value.

4.2.2 Time sweep

Storage modulus evolution

The storage and loss modulus of cements were observed over a period of one hour at constant frequency of 1 Hz and strain of 0.06% in order to study the effect of hydration kinetics on the rigidification process of cement paste. The storage modulus evolutions over time for the four cements with and without SP are shown in Figure 4.20 through Figure 4.22. The time scale for each sample shown in these figures is the same, to indicate clearly the differences in their rigidification. Also, each left graph is accompanied by its corresponding right figure in semi-log scale to illustrate the three regions of hydration kinetic of cement paste: retardation, rapid acceleration and the plateau.

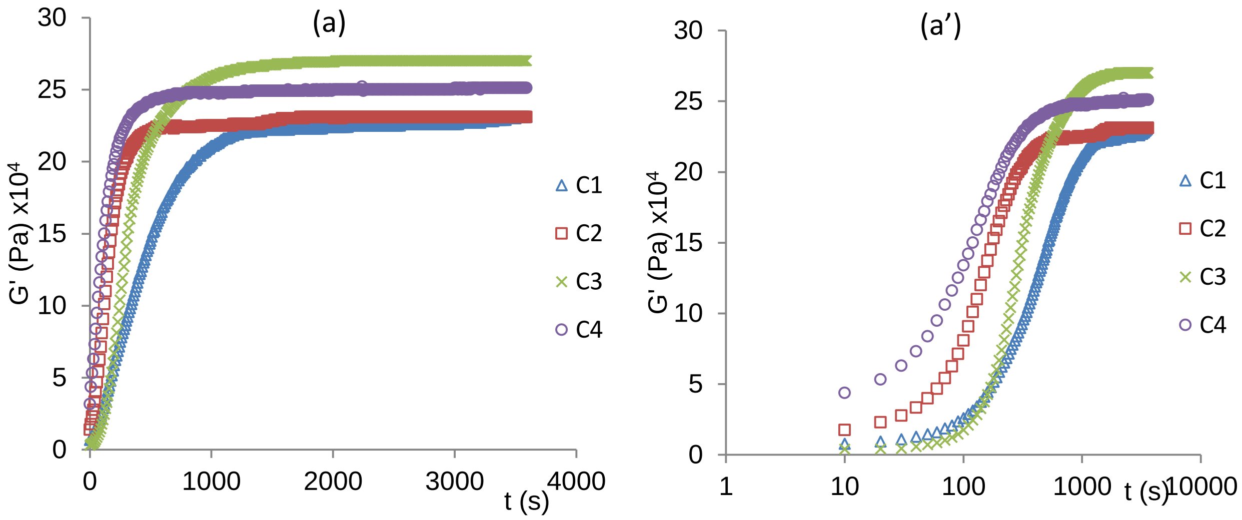


Figure 4.20: Storage modulus evolution for all cements without SP

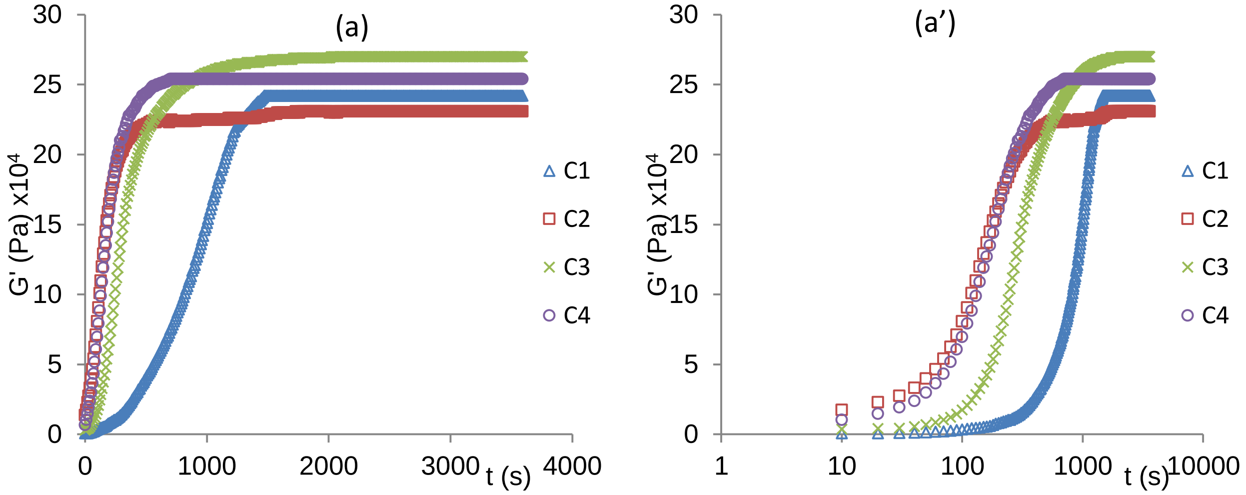


Figure 4.21: Storage modulus evolution for all cements with SP1 (0.3%)

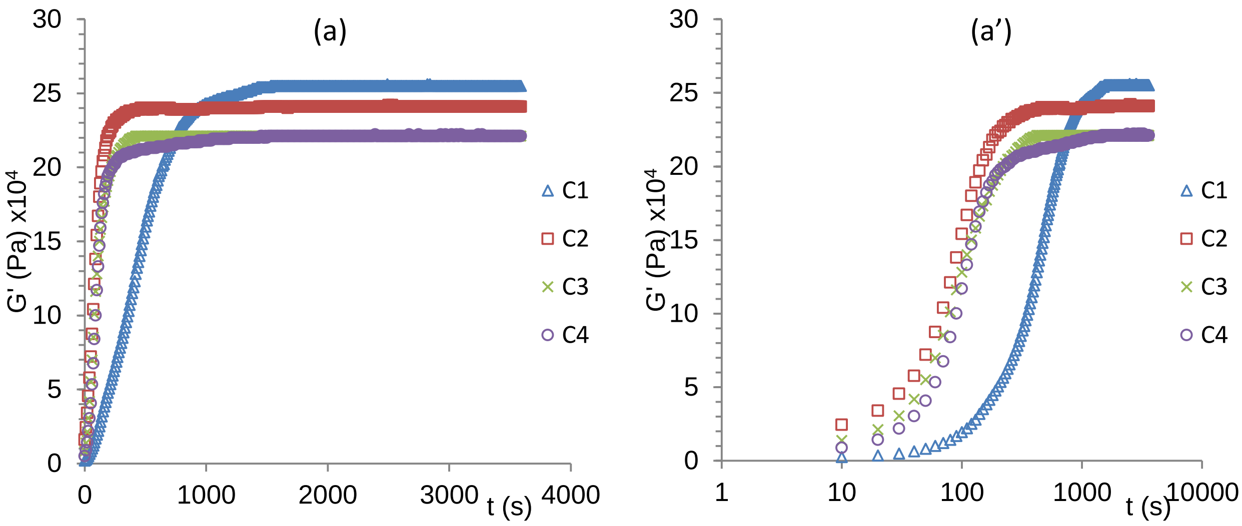


Figure 4.22: Storage modulus evolution for all cements with SP2 (0.3%)

The cements reached the plateau differently in terms of time and value of G’. This plateau occurred for Cements C2 and C4, with and without SPs, after an average time of 10 minutes of hydration. However, Cements C1 and C3 without SP reached a plateau after an average time of 20 minutes and the same time was recorded for these cements in the presence of SP1. With the addition of SP2, Cement C3 took almost 10 minutes to reach its plateau, while Cement C1 took approximately 20 minutes.

It is worth noting that this plateau was not a result of ‘slip effect’ for three reasons: firstly, the roughened plate geometry used minimises the occurrence of slip; secondly, the fact that the cements reached their plateau differently indicates that this was due to the effect of hydration; and finally, the modulus values recorded during experiments were in agreement with those reported in the literature for suspensions (Kirby & Lewis, 2004).

In the absence of SPs, the initial value of G’ for Cement C3 was the lowest, estimated at 4 kPa, and the highest value was with Cement C4: 44 kPa. However, Cement C3 reached the plateau with the highest value of G’, while Cement C1 experienced the lowest G’ value in the plateau zone.

There hydration kinetics time of cement pastes with and without SP differed, and these hydration times were prolonged with the addition of SPs. In all cases, Cement C4 experienced the shortest time of hydration before it reached its plateau, followed by Cement C2 and Cement C3, with Cement C1 experiencing the longest time of hydration.

SP added to the cement paste resulted in a decrease in the initial value of G’ and an increase of hydration time to reach the plateau. For instance, in the presence of SP1, Cement C1 exhibited the longest time of hydration to reach its plateau, followed by Cement C3. However, Cement C3 achieved the highest G’ value in the plateau interval and Cement C2 the lowest value in the same interval.

The introduction of SP2 caused Cement C1 to exhibit the highest value of G’ in the equilibrium interval, while Cements C4 and C3 resulted in the lowest values in the same region. Based on the observed rigidification trends of each cement under all the conditions, it is proposed that the setting process can be described by an equation of the self-acceleration type (Malkin & Kulichikhin, n.d.) fitted to the data.

Loss modulus development

The loss moduli of cements in both conditions of SPs are presented in Figure 4.23.

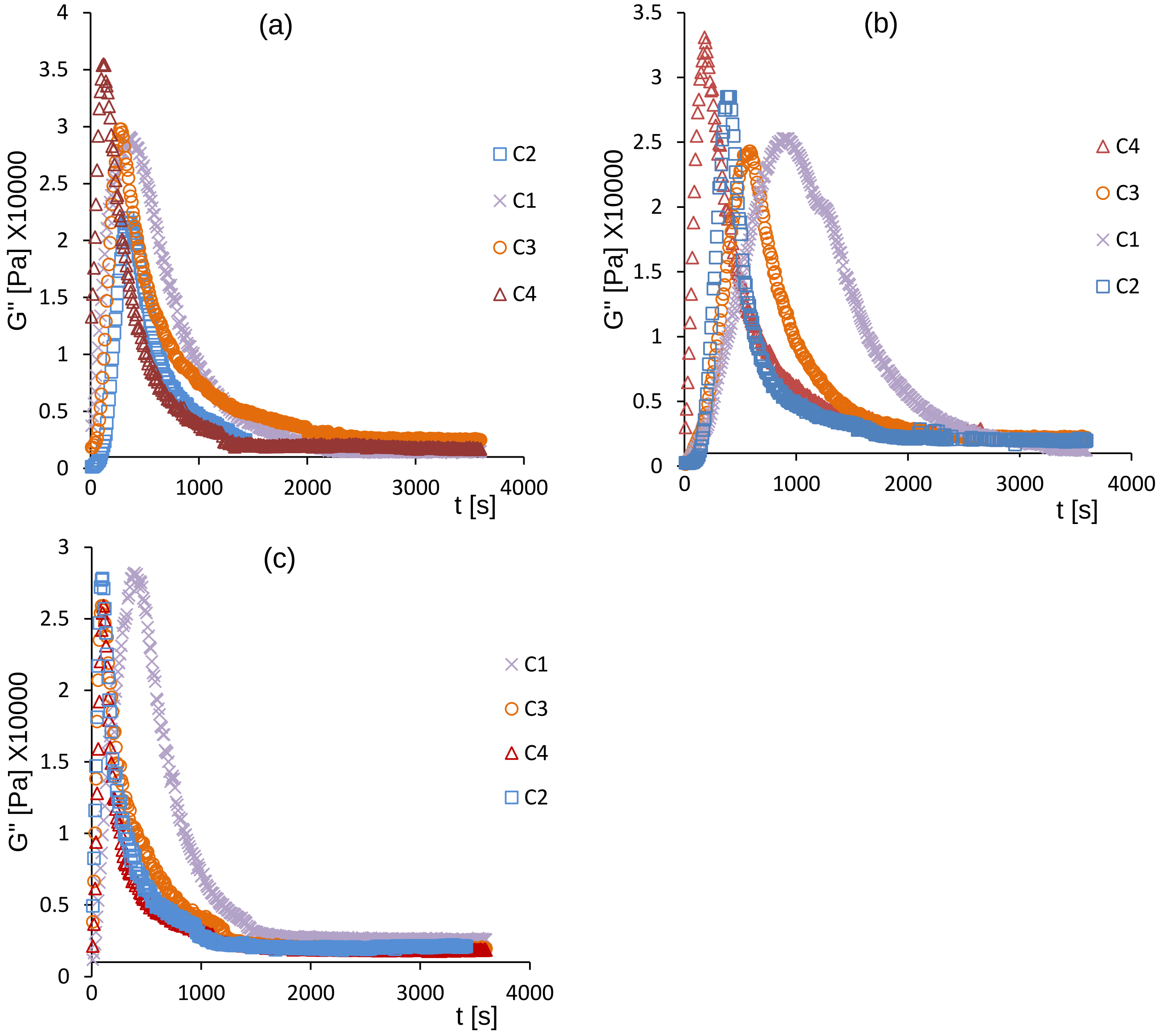


Figure 4.23: Loss modulus evolution for the all cements: (a) without SP; (b) with SP1 (0.3%); and (c) with SP2 (0.3%)

It is clear that cements exhibit differences in their loss moduli development.

Particular focus was on the time spent for each cement (in the presence and absence of SP) to reach its peak.

In the cases where there were no SPs in cement paste, Cement C1 exhibited the highest value of G” peak time at 310 seconds, while Cement C4 had the lowest value at about 100 seconds. Cement C2 and C3 reached their peaks at 130 seconds and 200 seconds respectively.

The addition of SP in cement paste extended the peak times of all cements. In the presence of SP2, all cements seemed to reach their peak time at the same time, averaging at about 100 seconds, except for Cement C1 that attained its peak after 380 seconds. SP1 affected cements differently. Cement C1 reached a maximum value at 930 seconds, Cement C2 at 340 seconds, Cement C3 at 530 seconds, and Cement C4 at 140 seconds. Table 4.10 gives a summary of these peak time values for each cement, both with and without SP.

Table 4.10: Loss moduli peak times of cements with and without SP (0.3%)

	G” PEAK TIME [s]		
Cements	**Without SP**	**With SP1**	**With SP2**
C1	310	930	380
C2	130	340	100
C3	200	530	120
C4	100	140	120

4.3 Thixotropy of cement paste

The thixotropy areas, referred to as the energy required to break the structure formed within cement paste, were calculated from the hysteresis loops as given in section 4.1.2. These areas were obtained at each resting time in order to estimate the rate of rebuilding of each cement in the presence and absence of SP. Table 4.11 gives the thixotropy areas of cements without SP.

Table 4.11: Thixotropy area at different resting times of all cements without SP

	Thixotropy area [Pa/s] of cements without SP			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**214**	**208**	**425**	**294**
5	**238**	**285**	**430**	**316**
10	**266**	**441**	**435**	**366**
15	**328**	**560**	**450**	**437**

In the absence of SP, Cement C3 had the highest thixotropy area values that did not significantly change over time as compared to the other cements. In general, Cement C1 had the lowest values of thixotropy areas. The values of thixotropy area for cements in the presence of SP1 are presented in Table 4.12

Table 4.12: Thixotropy area at different resting times of all cements with SP1 (0.3%)

	Thixotropy area [Pa/s] of cements with SP1			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**-**	**72**	**171**	**84**
5	**-**	**138**	**183**	**104**
10	**-**	**261**	**185**	**172**
15	**-**	**316**	**193**	**206**

In the presence of SP1, Cement C1 is an exception because there is no evidence of the structure formation during this period in this cement. This can also be predicted from the rheological data because it behaves as a simple Newtonian fluid. The effect of SP2 on the thixotropy area of cement paste is illustrated in Table 4.13.

Table 4.13: Thixotropy areas at different resting times of all cements with SP2 (0.3%)

	Thixotropy area [Pa/s] of cements with SP2			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**134**	**240**	**174**	**249**
5	**136**	**278**	**174**	**291**
10	**148**	**301**	**187**	**340**
15	**169**	**369**	**199**	**350**

In the presence of SP2, Cement C1 and C3 did not present significant change in the interval between one and five minutes of resting time. As a general observation in all cases, these thixotropy areas increased as the resting time increased.

4.4 Conclusion

The flow properties of cement paste were investigated by determining the yield stress and viscosity values in shearing mode from conventional flow curves (hysteresis loops) and the developed approach (construction of flow curve). The elastic properties of cement paste were assessed by calculating the yield stress values from the storage moduli versus amplitude sweep curves. The evolution of moduli were also monitored in order to quantify the effect of hydration on the rigidification of cement paste by using a rheokinetic model that is explained in Chapter 5. The thixotropy areas were obtained from the hysteresis loops at different resting times in order to estimate the rate of rebuilding of each cement.

Chapter 5 Discussion

This present section evaluates and discusses the results as presented in Chapter 4. The effect of SPs on flow properties and elastic properties of cement paste are discussed, as well as the impact of SPs on cement paste thixotropy behaviour. Yield stress values obtained by constructing flow curves and amplitude sweeps are compared to assess the effectiveness of this new approach of evaluating rheological parameters of cement paste. The prediction of cement paste rigidification in the early age of hydration is attempted by fitting experimental data by a kinetic model of self-acceleration. Finally, the effect of cement characteristics on the observed rheological behaviour of cement pastes with and without SP is evaluated.

5.1 Flow properties of cement paste

5.1.1 Viscosity kinetics

The kinetics of viscosity is presented in Figure 4.1. Figure 4.3 showed that at constant shear rate, the viscosity of cement paste is not constant. Referring to section 3.2, this seems to be controversial in regard to the way rheological parameters have been assessed in the previous literature when using constitutive equations such as the Herschel Bulkley model or the Bingham model. When using rheological models to evaluate the yield stress and the apparent viscosity of non-Newtonian fluids, the apparent viscosity is assumed to be constant over time at any constant shear rate. This was not observed with cement pastes. Therefore, the determination of cement paste rheological parameters requires a single value of viscosity to be obtained at constant shear rate.

The characterisation of cement paste by constructing flow curves was based on this, as this approach provides values of both yield stress and viscosity in time that can be related to the changes that occur in the microstructure during hydration.

The viscosity evolution of cement pastes are obtained in shearing mode. Many researchers agree that in this mode, the microstructure of the material is destroyed and thus cannot be used to obtain information about the microstructure of cement paste (Nachbaur *et al.*, 2001).

Roussel (2005) was one such reseacher who observed that since cement is a thixotropic material, the structure breakdown and structure rebuilding occurred at the same time. During the breakdown phase, the particles of cement orientate themselves in the line of flow, resulting in a decrease in viscosity. The reorganisation of particles takes time and defines the rebuilding phase characterised by the increase in viscosity. Lapasin *et al.* (1979) and Otsubo *et al.* (1980)

demonstrated that the first phase depends on the applied constant shear rate which happens in a short period of time and continues until equilibrium is reached, while the second phase depends on the hydration process (Jarny *et al.,* 2008).

The kinetics of cement paste viscosity obtained in this study were in agreement with these researchers, since the viscosity at each constant shear rate was increasing over time. However, only the second phase was observed during the experiments, suggesting that the first phase, where the microstructure is destroyed, happened during the pre-shearing phase that lasted 10 seconds at 50/s. This pre-shearing time was determined to be sufficient for cement paste to reach its steady flow (Geiker *et al.*, 2002).

One would therefore, assume, that the effect of hydration was more pronounced than the effect of structure breakdown. Hence, this technique can be used to investigate the effect of hydration on cement paste rheological behaviour, notably the loss of cement paste workability (yield stress development) and loss of cement paste fluidity (plastic viscosity development) (Nachbaur *et al.,* 2001; Hanehara & Yamada, 1999). The same behaviour of viscosity development as described above was observed when SP was added to the cement paste. There was a plateau at the beginning of each viscosity-time curve, the length of which depended on the interaction of cement and SP used. This plateau would be the continuity of the equilibrium state reached in the first phase of viscosity evolution due to the electrostatic repulsion effect of SP that retards the hydration process (Bhatty, 1987; Kim *et al.,* 2000)**.**

A comparison of Figure 4.2 and Figure 4.3 demonstrates that during the second phase, for all cements with SPs, the viscosity starts increasing about 60 seconds after the experiment started.

5.1.2 Effect of SP on yield stress development

The construction of flow curves could be used to monitor the development of yield stress and the apparent viscosity of cement paste. A single value of yield stress is not enough to characterise the flow behaviour of cement paste. The yield stress corresponds to the amount of stress required to break the internal structure developed by the hydration process within the cement paste. In as much as this rheological parameter depends strongly on the hydration, a phenomenon that evolves with time, its value has to be determined over time. In other words, at each point in time as the hydration develops, the stress required to break the formed structure has to be determined. With this approach of estimating the yield stress, it was possible to follow the evolution of yield stress and apparent viscosity over time as well as the effect of SP.

For instance, in Table 4.1, all cements exhibit an increase in their yield stress values as time of hydration increases. Table 4.2 and Table 4.3 show the yield stress values of superplasticised cement paste. Although these values are decreased compared to their corresponding unsuperplasticised values, yet they also increased with the hydration time. Figure 4.8 - Figure 4.12 illustrate the evolution of these rheological parameters where the loss of workability and fluidity of cement paste could be seen by considering the slope and values of, respectively, yield stress development and viscosity changes. The effect of SPs on yield stress development and thus on the workability of cement paste is well depicted in Figure 5.1.

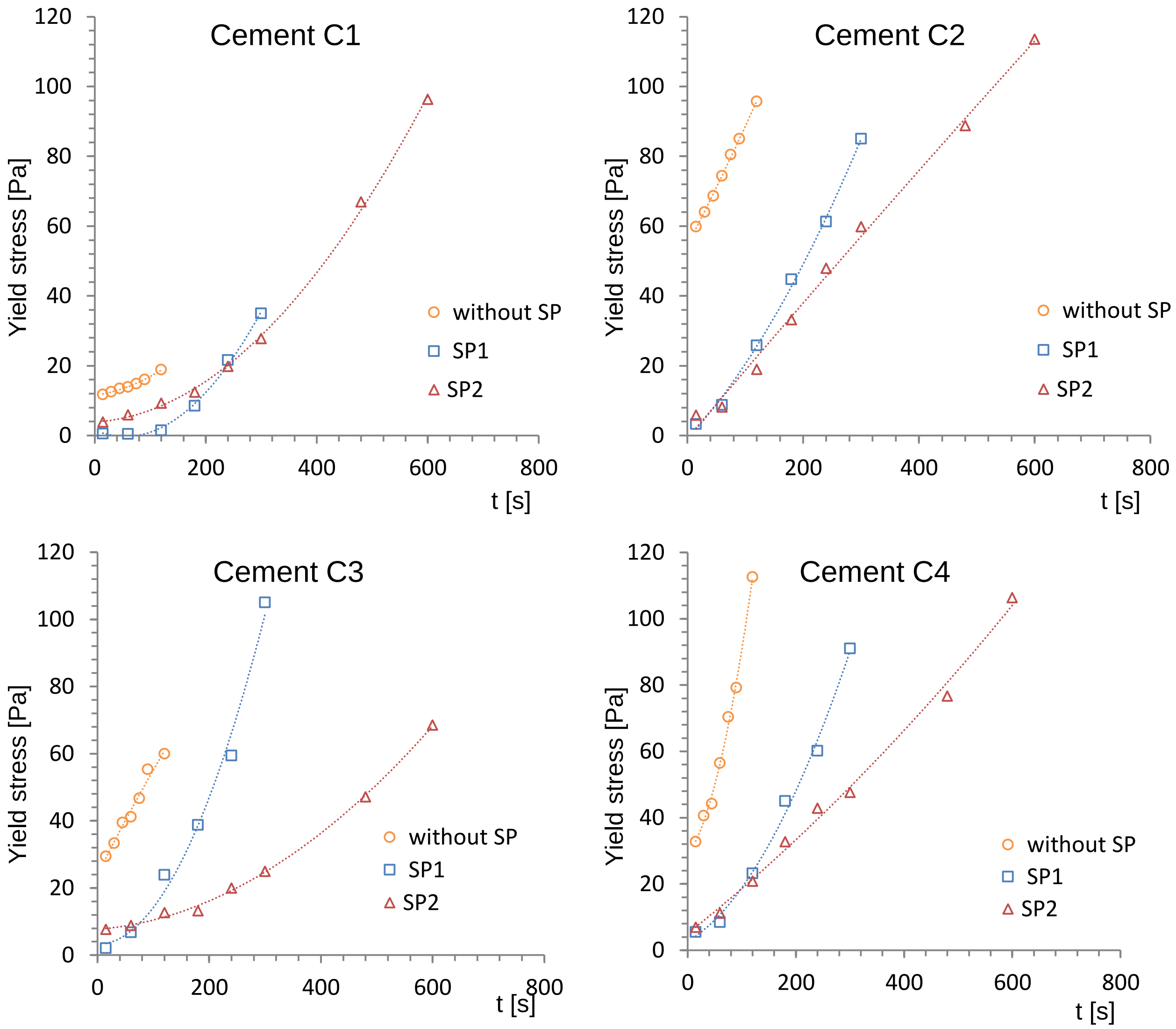


Figure 5.1: Effect of SP on cement yield stress development of cement paste

In general, it is clear that the introduction of SPs in cement significantly reduced the yield stress values. In the absence of SP, Cement C1 had a low slope resulting in flatter yield stress development, indicating a small loss in cement paste workability, because the cement remained wet for a long period of time. Cement C4, however, with a steep slope, resulted in a rapid yield stress development that indicated a fast loss in cement paste workability. Both SP1 and SP2 had a strong effect on Cements C1 and C3. In fact, a long delay (illustrated by the plateau) in yield stress evolution was seen in Cement C1 when using SP1, whereas the same behaviour was noticed in Cement C3 in the presence of SP2.

In the literature, the flow properties of cement paste were investigated using the conventional flow curves method from hysteresis loop (Banfill, 2006)**.** Yield stress values from conventional flow curves for each cement in the presence and absence of SP are presented in Table 5.1. The procedures followed to obtain these values are as presented in sections 2.3.7, 3.2 and 3.3.

Table 5.1: Yield stress values determined from hysteresis loops

	Yield stress [Pa] of cements without SP			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**9**	**20**	**20**	**25**
5	**9**	**20**	**20**	**25**
10	**10**	**20**	**23**	**32**
15	**10**	**27**	**23**	**33**
	Yield stress [Pa] of cements with SP1			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**0**	**2**	**0.1**	**11**
5	**0**	**2**	**0.1**	**13**
10	**0**	**3**	**0.2**	**13**
15	**0**	**4**	**0.2**	**14**
	Yield stress [Pa] of cements with SP2			
Resting time[min]	**C1**	**C2**	**C3**	**C4**
1	**1**	**3**	**0**	**5**
5	**1**	**3**	**0**	**6**
10	**1**	**5**	**0**	**8**
15	**1**	**5**	**0.2**	**8**

Examining these yield stress values, the following should be noted: firstly, the linear approximation is valid and establishes the values related to the initial state of a sample; and secondly, the yield stress values depend on the resting time between upward and downward branches, though this dependence is not strong for the first five minutes of rest, and even up to 15 minutes.

In fact, there is no important change in cement paste yield stress values that occurs after 15 minutes of resting time. In other words, these yield stress values measured after one minute of resting time are almost equal to the values measured after 15 minutes. The values dropped even more drastically with the presence of SP within the pastes and don’t change over time.

This seems rather controversial when taking the effect of hydration into consideration. After 15 minutes resting time, the hydration should have affected the mechanical properties of the cement paste, resulting in reasonable growth of the yield stress values. Possibly, the effect of shearing during measurements was more pronounced, breaking continuously the developed structure of the cement paste. These results are rather disappointing and create some doubts as to the physical sense and reliability of the results with the application of this method.

For this reason, it is clear that the hydration and the microstructure of the cement paste are disturbed during the experiments; hence, this method should not be used to monitor the growth of yield stress values.

5.1.3 Effect of SP on plastic viscosity evolution

The values of plastic viscosity for each cement with and without SP are illustrated in Figure 4.9, Figure 4.11 and Figure 4.13 and summarised in Table 4.1 through Table 4.3. The effect of SP on plastic viscosity of cement pastes is shown in Figure 5.2.

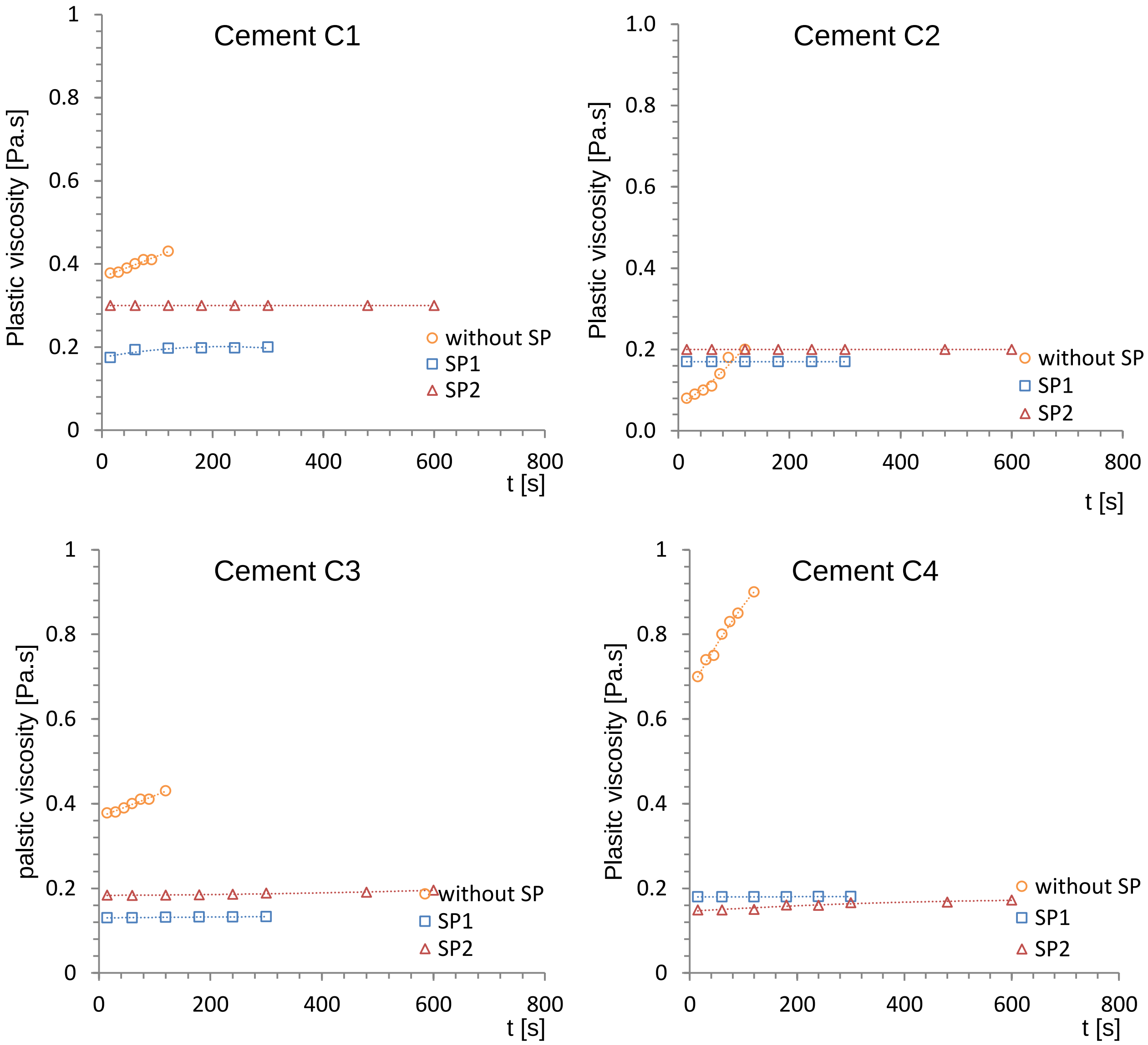


Figure 5.2: Effect of SP on cement paste viscosity development

It is clear that all cements are affected by the addition of SP into the paste in terms of decreasing the plastic viscosity, thereby improving the fluidity of cement paste. Similar behaviour has been observed by Asaga and Roy (1980) and Hanehara and Yamada (1999). In general, SP1 seems to have a greater effect on all cements than SP2. This difference is more evident in Cements C1 and C3. Cement C2 exhibited a specific behaviour with the addition of SPs. In fact, in the beginning of hydration, its plastic viscosity increases when SP is added and remains constant throughout the process. It was noticed that SPs did not affect this cement significantly, since there was little difference observed between cases where there was no SP and when SPs were added. Both SP1 and SP2 impacted Cement C4 in the same way, reducing its plastic viscosity drastically to almost identical values.

In the absence of SP, the plastic viscosity of cements increased over time for all cements. This behaviour was also observed by Justnes and Vikan (2005) for a number of cements. With the addition of SPs, the increase in plastic viscosity for each cement was not significant as time evolved. Cement C4, in the absence of SP, exhibited the steepest slope of plastic viscosity growth, implying a rapid fluidity loss, while Cement C2 exhibited small value of plastic viscosities with a much flatter slope as clearly shown in Figure 4.9, indicating a slow fluidity loss. Cement C1 showed a great fluidity loss as compared to Cement C3.

With the addition of SP, the plastic viscosity values were significantly reduced and remained nearly constant over time, as indicated by the nearly flat slope implying a slow rate of fluidity loss. Consequently, cements remained fluid for a longer period of time. Similar behaviour was observed by Justnes and Vikan (2005).

5.2 Elastic properties of cement paste

The dynamic mode (oscillatory mode) rheology was used to determine the yield stress values of cement paste using the amplitude sweep technique, while the kinetic of cement paste microstructure was monitored using the time sweep technique.

5.2.1 Effect of SP on yield stress values

The value of yield stress determined in oscillatory mode gives the information concerning the continuous changes of cement paste structure that occur during hydration (Min *et al.*, 1993; Nehdi & Al Martini, 2009). Table 5.2 presents the values of yield stress for each cement in the presence and absence of SP.

Table 5.2: Yield stress values of cements with and without SP determined by amplitude sweep

	CEMENT WITHOUT SP			
	C1	**C2**	**C3**	**C4**
Yield stress [Pa]	**19**	**102**	**68**	**117**
	CEMENT WITH SP1 [Pa]			
	C1	**C2**	**C3**	**C4**
Yield stress [Pa]	**4**	**50**	**23**	**100**
	CEMENT WITH SP2 [Pa]			
	C1	**C2**	**C3**	**C4**
Yield stress [Pa]	**10**	**73**	**14**	**53**

These values are a true reflection of the effect of hydration on cement paste based on the fact that the kinetic reaction of cement compound was not disturbed by this technique. The effect of SPs on each cement was observed in such a way that the individual yield stress values were reduced. Cements C1 and C2 seemed to be more affected by SP1, while Cements C3 and C4 were more affected by SP2.

5.2.2 Kinetics of cement paste hydration

Storage modulus evolution

The aim was to investigate the kinetics of hydration and to propose a general kinetic equation that could be used to describe the rigidification process of cement paste.

The rheokinetic modelling approach used to follow the curing mechanism of polymers (Malkin & Kulichikhin, n.d.) was used for the first time to describe the initial hydration of cement paste. The evolution of cement paste microstructure can be followed either by monitoring the growth of yield stress as explained previously, or by monitoring the growth of the elastic modulus (Roussel *et al.*, 2012). The considered method consists of predicting the time dependence of the elastic modulus (within the linear viscoelasticity domain) by a kinetic equation of the self-acceleration type and fitting the equation to the experimental data.

Figure 4.30 presentes the evolution of storage moduli that indicate the time dependency of cement pastes. These rigidification trends can be described by Equation 5.1:

$$\frac{d\beta}{dt} = \frac{1}{\theta}(1-\beta)(1+K\beta) \tag{5.1}$$

where β is some measure of the chemical transformation; θ is the characteristic time constant determining the starting rate equal to θ^{-1}; K is the dimensionless parameter reflecting the rate of self-acceleration; and t is time. Integrating Equation 5.1 gives:

$$\frac{1}{1+K}\left[-\ln(1-\beta)+\ln(1+K\beta)\right] = \frac{t}{\theta} \tag{5.2}$$

It can be seen from Equation 5.2 that at $t = 0$, $\beta = 0$. The parameters of the kinetic law, Equation 5.2, for each material under study can be derived by optimal fitting of K and β to the experimental data. Practically speaking, K can be found via the position at which the rate is maximum (i.e. via the value of β_m at which $d^2\beta/dt^2 = 0$). At this point:

$$K = \frac{1}{1 - 2\beta_m} \tag{5.3}$$

Then θ can be found either via the starting rate of the process (initial slope of the graph) or can be calculated via any pair of t and β values in the middle or close to the origin of the kinetic curve. When using the experimental storage modulus data, β is understood to be as follows:

$$\beta(t) = \frac{G(t) - G_0}{G_\infty - G_0} \tag{5.4}$$

Actually, β is the ratio of the current storage modulus $G(t)$ to the plateau modulus (end of the curve) G_∞, assuming the initial modulus G_0 to equals zero. Equation 5.5 allows us to estimate the complete rigidification time, T^* , assuming that $\beta = 0.95$:

$$T^* \cong \frac{\theta}{1+K}[3 + \ln(1+K)] \tag{5.5}$$

When testing commercial cement types and superplasticisers, reproducibility or scatter in experimental data have an accuracy of ± 10% at best, so the kinetic constant too can be determined only within these limits.

Further discussion of the kinetics of cement rigidification focuses on evaluation of the dependency of the two kinetics constants θ, which characterise the duration of the measured hydration time in the dormant phase, and K, the rate of self-acceleration constant which determines the final part of the kinetic curve, for plasticised and unplasticised cement pastes. This approach makes the comparison of different cement compositions and the role of superplasticiser more quantitative.
Figure 5.3 clearly illustrates the difference in the self-acceleration constant of both superplasticised and unsuperplasticised cement pastes.

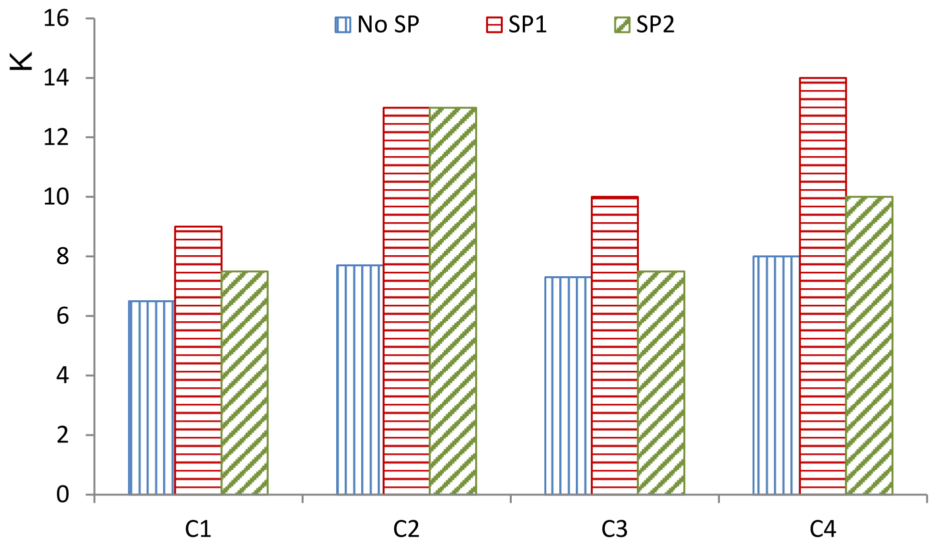
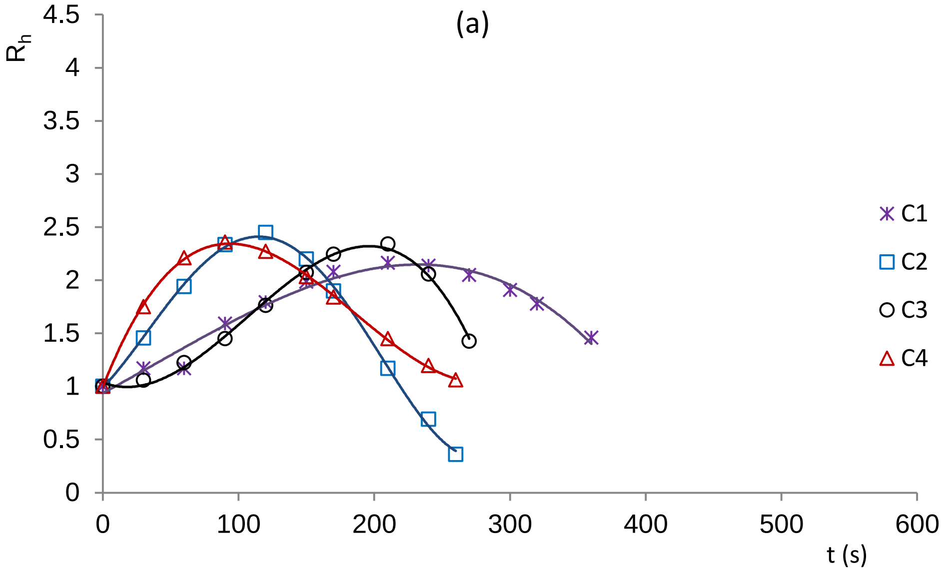
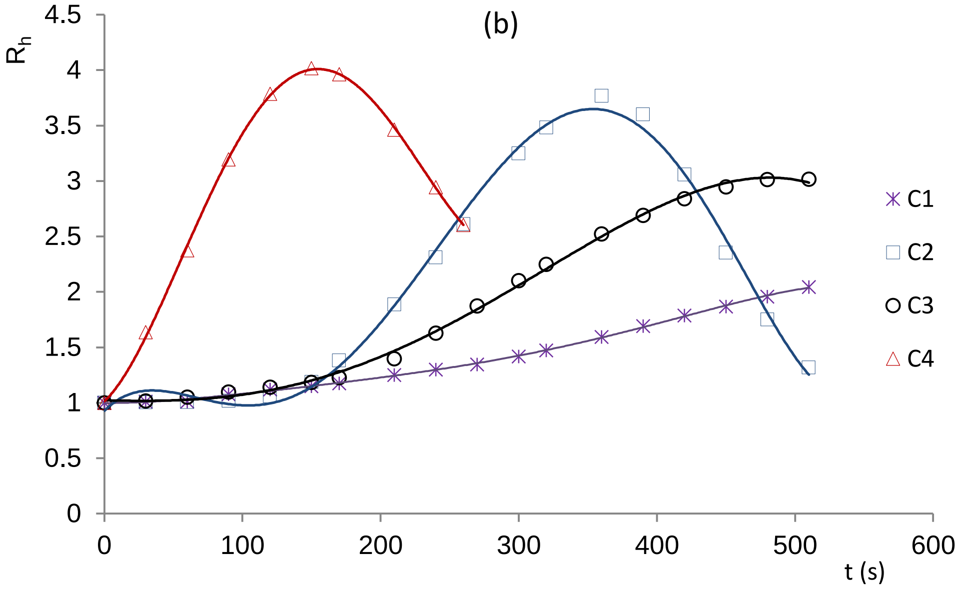


Figure 5.3: Self-acceleration constants for all cements with and without SP at 0.3%

In the absence of SP, there was no much diference observed in the self-accelartaion values of cements. With the addition of SP, Cements C2 and C4 had the highest values of the self-acceleration coefficient and C1 and C3 the lowest. In general, the presence of SP in the paste increased the values of the self-acceleration coefficient. SP1 had a greater effect on the rate of hydration than SP2 as the *K* values of cements with SP1 are higher than those with SP2.

All the differences observed from cements with and without SP in terms of their self- acceleration values could be an indication of the variations in the rate of hydration within the cement pastes as depicted by the relative rate of hydration (R_h) parameter determined from Equation 5.1 as $(1-\beta)(1+K\beta)$ and shown in Figure 5.4**.** Reduction of these experimental curves to the same starting point removes the influence of the initial rate of the process and clearly illustrates the role of the self-acceleration.


(a)
R_h
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
600
t (s)
C1
C2
C3
C4


(b)
R_h
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
600
t (s)
C1
C2
C3
C4

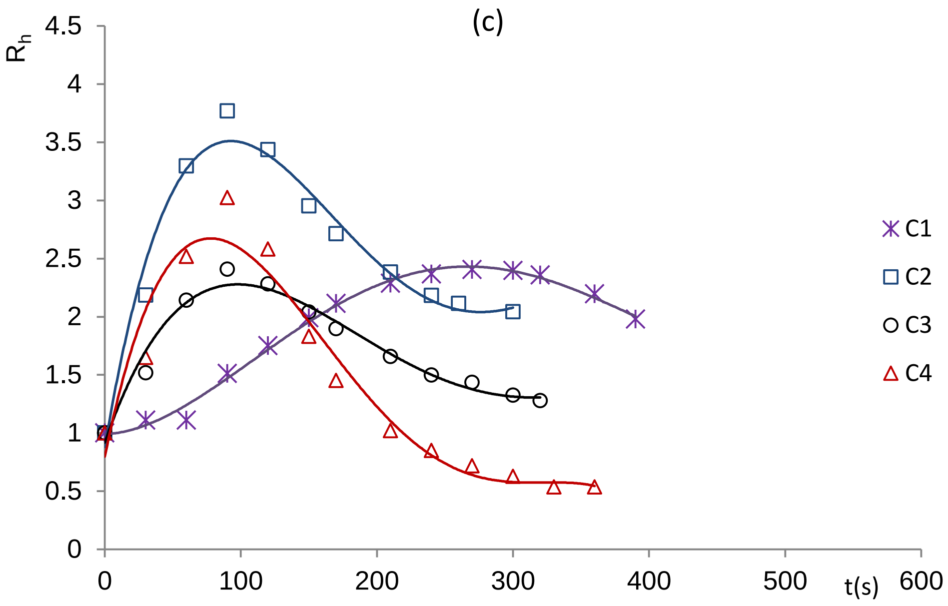


Figure 5.4: Relative rate of hydration of cements: (a) without SP; (b) with SP1 at 0.3%; and (c) with SP2 at 0.3%

This graphical presentation of the data (Figure 5.4) illustrates the self-acceleration character of the hydration kinetics for plasticised cements. It is therefore possible to assess the effectiveness of the SP when mixing with the different cements.It can be seen that the addition of SP increases the values and shifts the maxima of the kinetics curves out in time, thus prolonging the hydration process and slowing down the rate of the hydration within the cement paste. The retardation effect of SP1 is more pronounced than SP2. This effect is illustrated in Figure 5.5 which shows the increase in the characteristic time with the introduction of SP. The greater effect of SP1 on the cements as compared to SP2 can be seen distinctly.

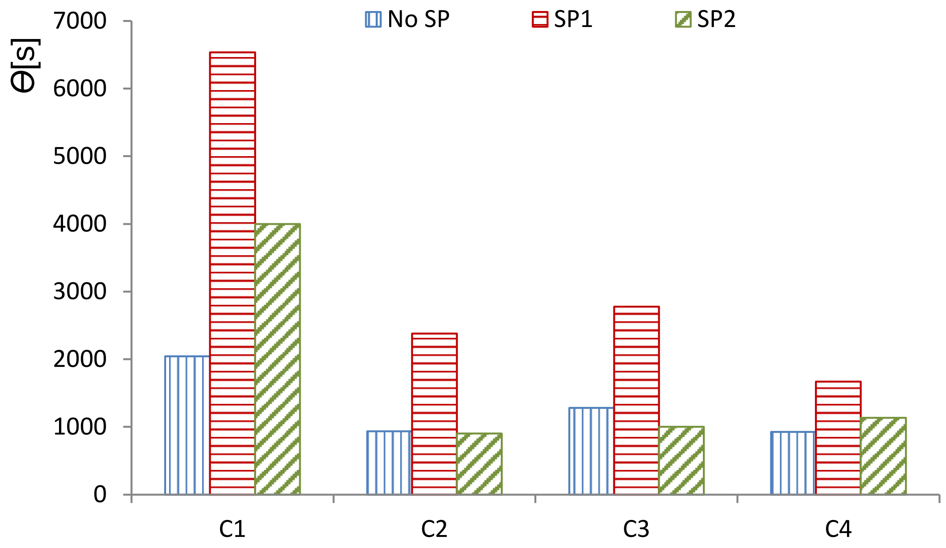


Figure 5.5: Duration of measured hydration in dormant phase expressed as characteristic time Θ for all cements with and without SPs at 0.3%

In the absence of SP, Cement C1 presented the highest characteristic time Θ followed by Cement C3 and Cements C2 and C4. This implies that Cements C1 and C3 took more time in their hydration process as compared to Cements C2 and C4. The addition of SP1 to the cement pastes caused Cement C1 to exhibit the highest value of Θ while Cement C4 presented the lowest value. The inclusion of SP2 did not have a major effect on the characteristic times of all cements as the characteristic time of these cements in the presence of SP2 were almost the same as in the case where there was no SP, the exception being Cement C1. This behaviour aligns with the previous observation concerning the rate of hydration of cements in Figure 5.4 showing clearly that cement with a low rate of hydration would result in long characteristic time as an indication of the length of the hydration time.

As a general observation, the presence of SP in cement pastes extended the characteristic time values during hydration, and SP1 had a greater effect on the cements than SP2. As a consequence of the dependencies of the constants Θ and *K* on the hydration kinetics of cement, the total time (*T**) for each cement to reach its plateau increases also with the addition of SP. In all cases the *T** values calculated using Equation 5.5 are in solid agreement with the experimentally observed duration of the process even taking into account some uncertainties in the estimation of the final point. The values of *T** are presented in Figure 5.6 and the comparison to the experimental data in Figure 5.7.

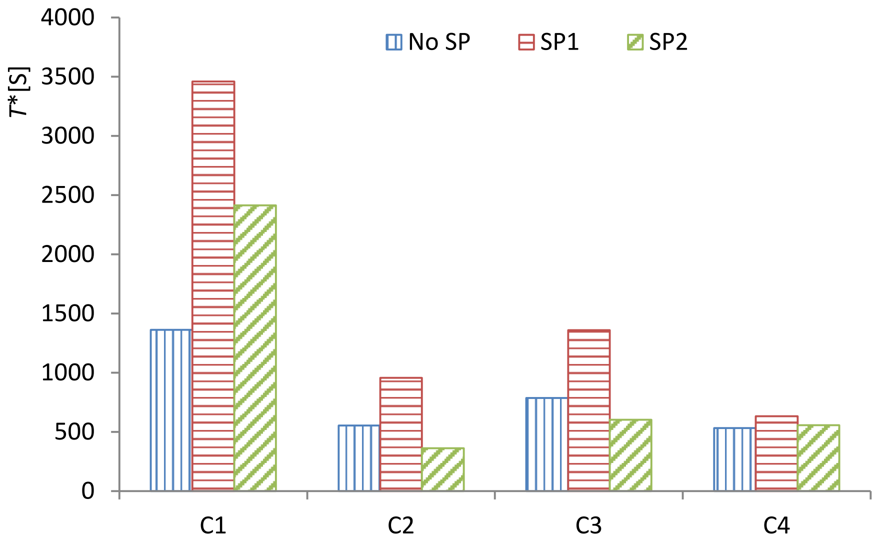
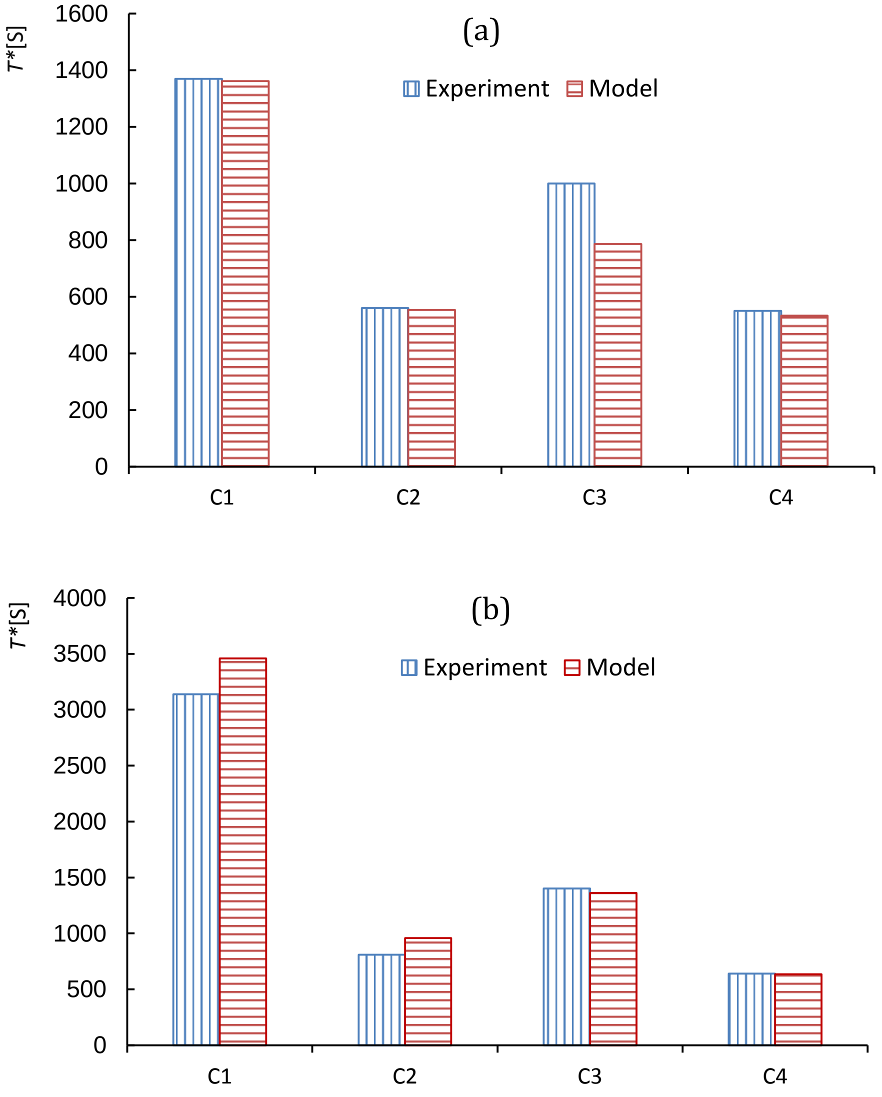


Figure 5.6: Values of *T** for all cements with and without SP



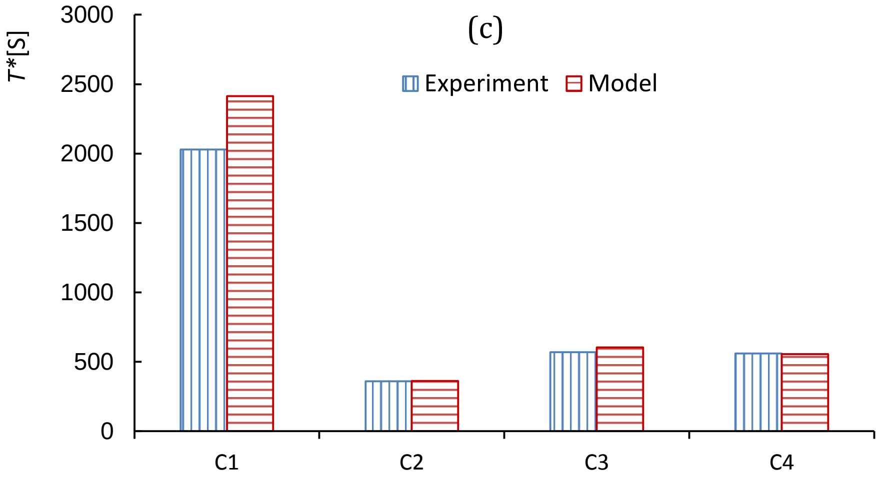


Figure 5.7: Comparison of *T** values to experimental values: (a) cements with no SP; (b) cements with SP1; and (c) cements with SP2

In the setting process of cement, it is very important to know the rate of hydration since the development of the cement microstructure strength depends on the hydration. Within this view, one can notice that the rheological characterisation of these cements, as determined by the proposed rheokinetic model, followed a trend so that in the absence of SP, Cements C4 and C2 showed the highest rate of hydration while Cements C1 and C3 had the lowest rate of hydration. With the addition of SP1, Cement C4 performed the highest rate of hydration, followed by Cements C2, C3 and C1. In the presence of SP2, Cements C2 and C4 showed the highest rate of hydration, whereas Cements C1 and C3 showed the lowest rate. These differences in rheological behaviour could be attributed to both physical and chemical characteristics of each cement, as per Table 3.1 through Table 3.3, affecting the strength development of cements for both SP.

Loss modulus evolution of cement paste

The loss moduli evolution of cements are presented in Figure 4.23 and the corresponding times to reach their peaks are tabulated in Table 4.10. It was also found that there is a relationship between these *G”* peak times and the coefficient *T** as determined by the rheokinetic model in Equation 5.5. Figure 5.8 gives the correlation of *T** and G’’ peak time of cements.

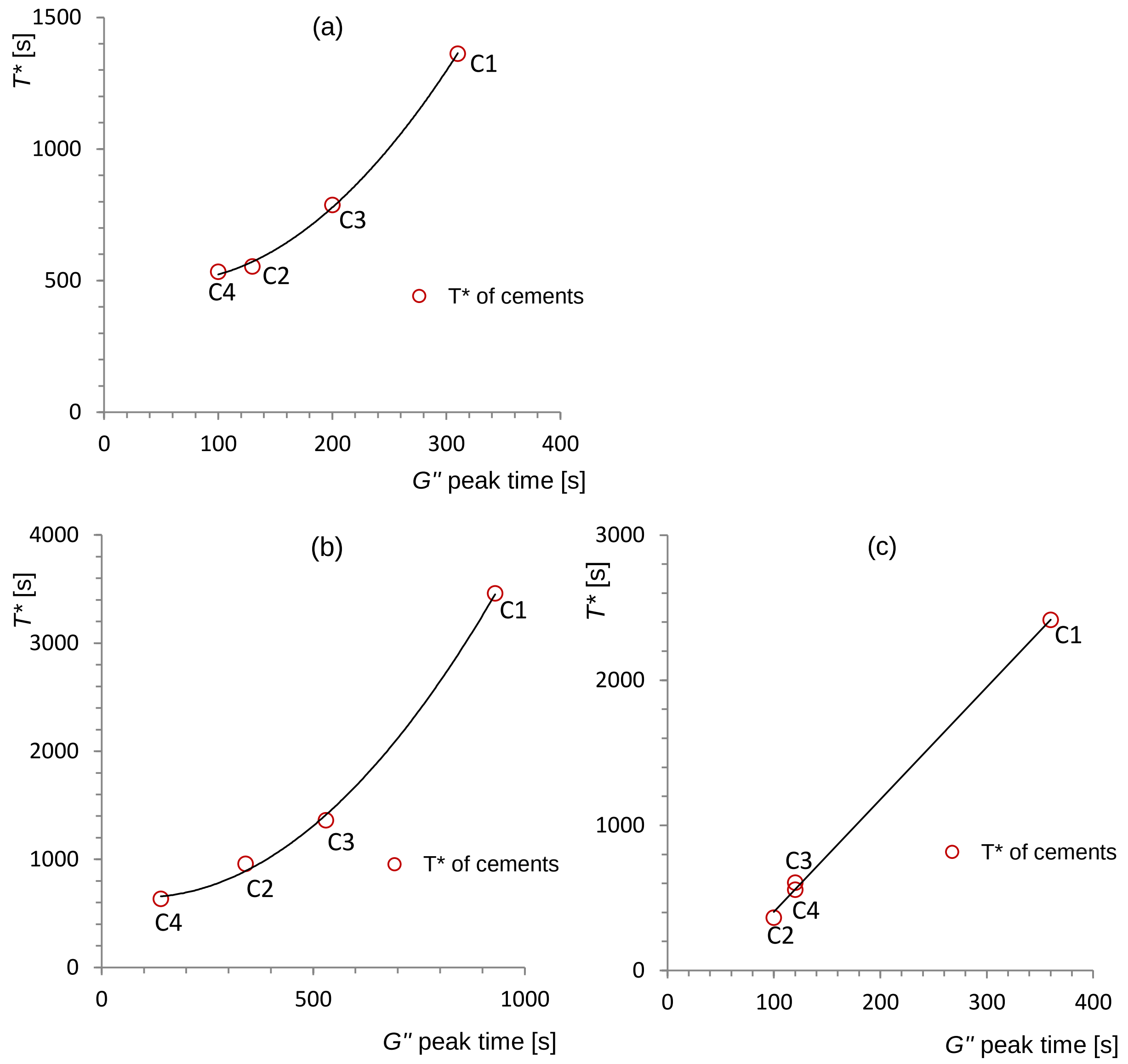


Figure 5.8: Correlation of *T** and *G''* peak times of cement: (a) without SP; (b) with SP1 (0.3%); and (c) with SP2 (0.3%)

Undeniably, the relationship that exists between *T** values and *G''* peak time values of cement pastes in the absence of SP and presence of SP1 is polynomial, while linear for cements with SP2.

5.3 Yield stress comparison for fresh cement paste

Three different techniques were used to estimate the rheological parameters of cement pastes: conventional flow curves (hysteresis loops), construction of flow curves and amplitude sweep.

The values of yield stress provided by each method for each cement, with and without SP, are compared in this section.

Since the yield stress of fresh cement paste depends on the kinetics of hydration, it is reasonable to compare the different methods by considering the same time of hydration at which the value of yield stress was obtained and determined by each method.

For constructing flow curves and hysteresis loops, the hydration time of interest was obtained directly from Table 4.1-Table 4.6. For amplitude sweep, an integration of the amplitude rate would provide the time of hydration at which the critical strain was reached and hence the yield stress value.

The yield stress values of the fresh cement pastes in the presence and absence of SP, as determined by each method, are presented in Figure 5.9 and Figure 5.10.

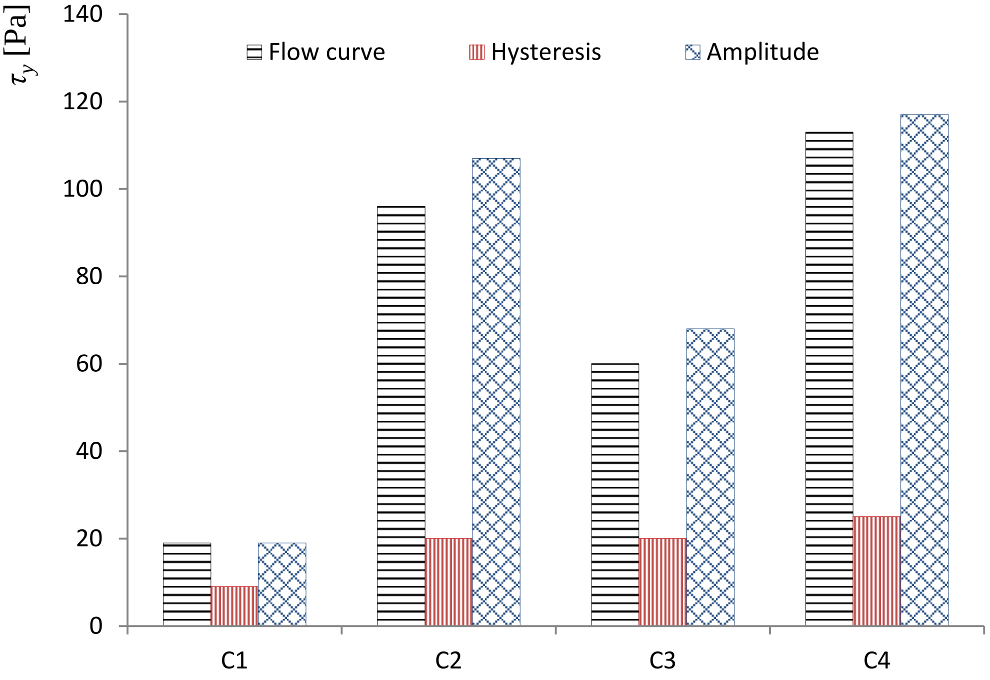


Figure 5.9: Yield stress comparison for fresh cements without SP

With no SP in the cement paste, the yield stress values estimated from constructing the flow curves were almost equal to those obtained by amplitude sweep, whereas those determined by hysteresis loops were very small compared to those from the two other methods.

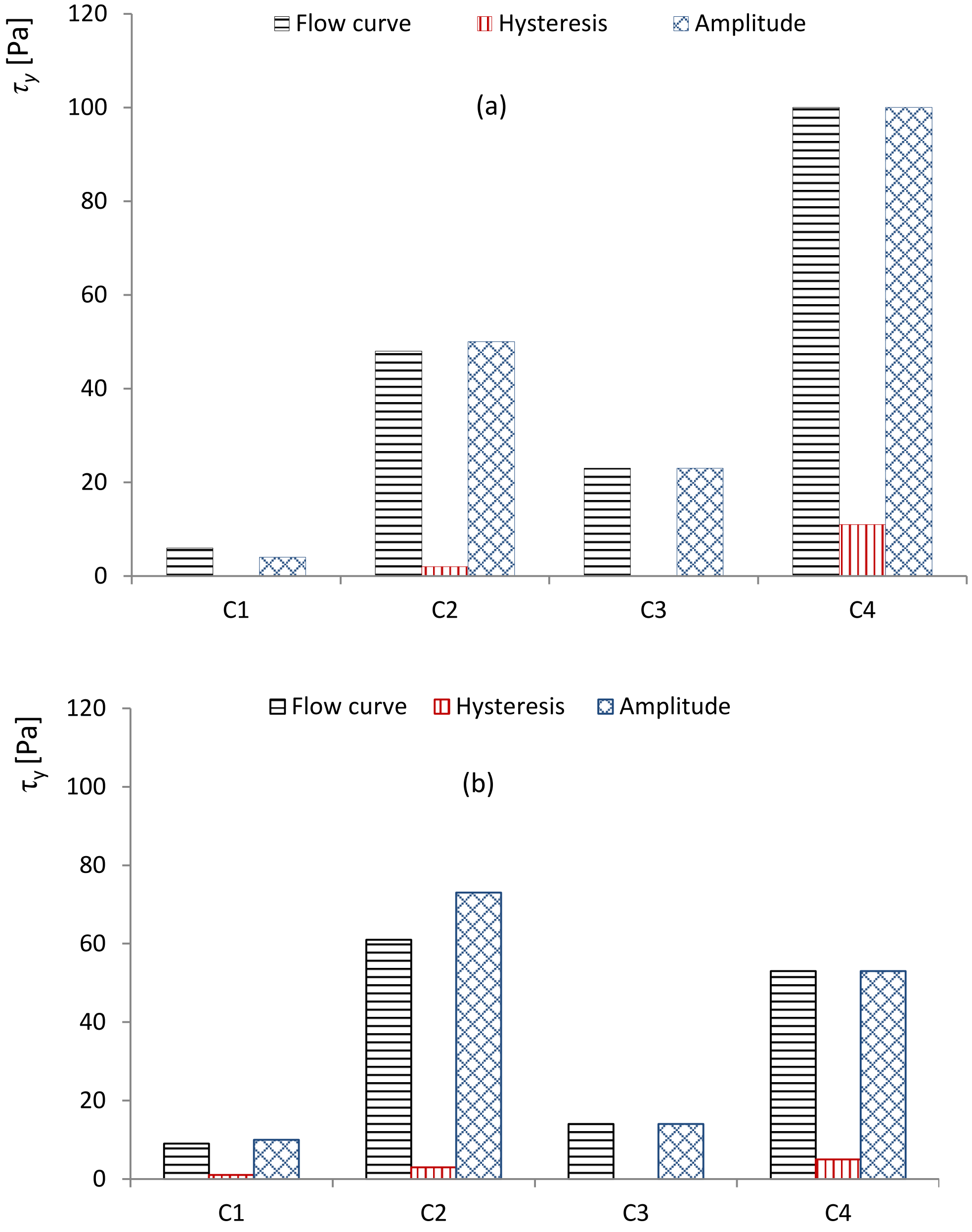


Figure 5.10: Yield stress comparison for fresh cement pastes with: (a) SP1 (0.3%); and (b) SP2 (0.3%)

Each method was able to depict the influence of SP in the cement paste based on the yield stress values determined. In fact, each method used indicated the decrease in yield stress values for each cement paste in the presence of SP compared to paste with no SP. However, the values determined by hysteresis loops were small compared to those determined by the amplitude sweep and constructing of flow curves. This could be explained by the fact that during the experiments, the structure of the material is continuously destroyed due to shearing. The pre-shearing at 50 s-1 for less than 15 s is sufficient to destroy the cement paste structure formed even after 15 minutes.

There was very little difference between yield stress values obtained from constructing the flow curves and those from amplitude sweep.

5.4 Effect of SP on thixotropy of cement paste

5.4.1 Thixotropy area of cement paste

The thixotropy areas of cement pastes were presented in Table 4.11 - Table 4.13. These areas define the energy required to break the structure formed within the cement paste (Quanji, 2010).

The effect of SP on the thixotropy of cement pastes is shown in Figure 5.11, where superplasticised cement pastes are compared to unsuperplasticised cement pastes.

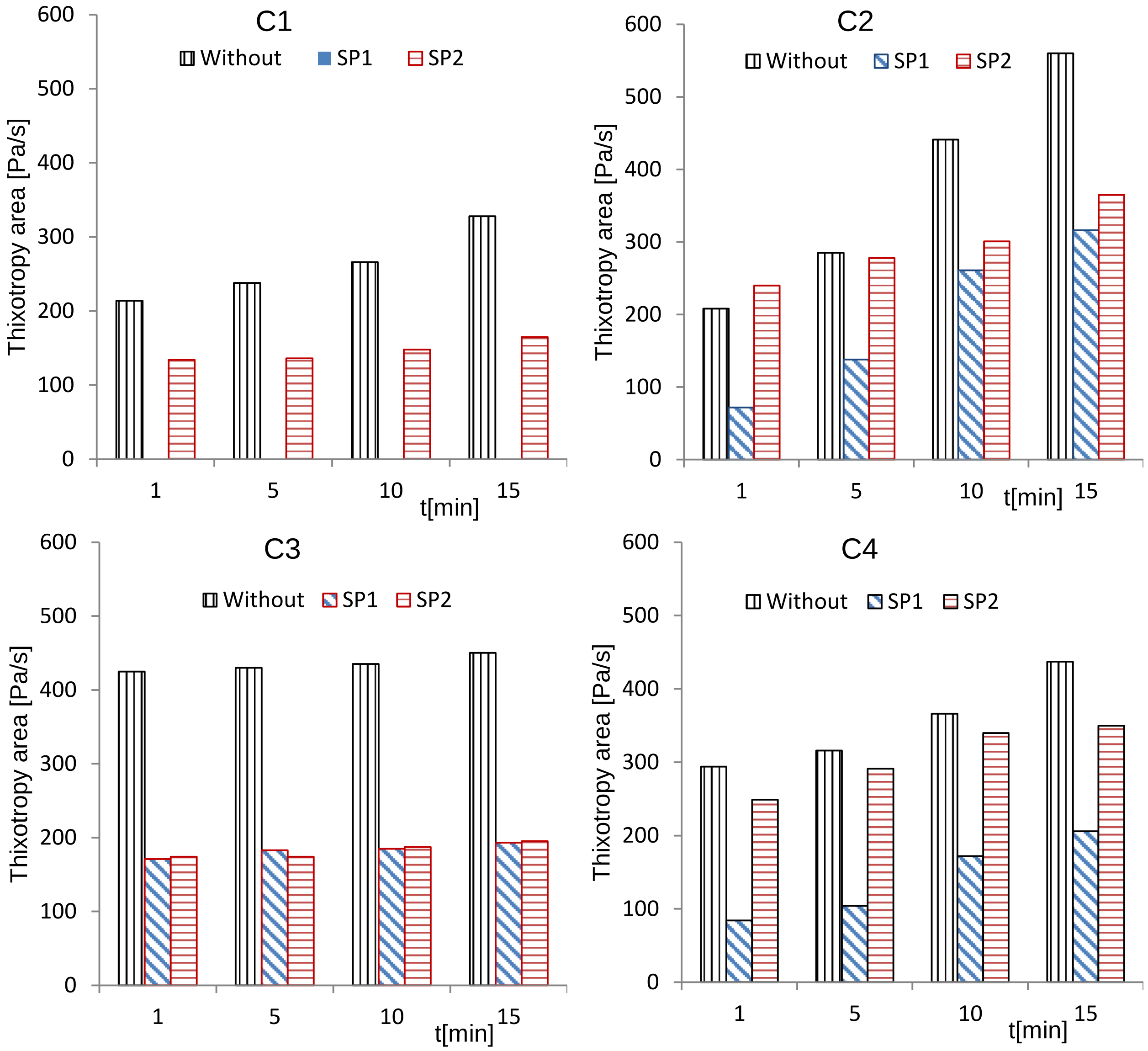


Figure 5.11: Thixotropy area change over time of cements with and without SP (0.30%)

As could be expected, the area of the thixotropic loops increases, along with the resting time, as a consequence of the continuous structure formation. Sample C1 in the presence of SP1 is an exception because there is no evidence of the structure formation during this period in this cement. This can also be predicted from the rheological data because it behaves as a simple Newtonian fluid. However, the efficiency of plasticising is different for the four cements. The effect of SP1 is very strong and evident for C2 and C4, whereas for Cement C3 the effect remains constant over time. The effect of SP2 on Cement C3 is similar as for SP1 but very strong on Cement C1. For Cements C2 and C4, the effect of SP2 could be noticed only after 10 minutes. In general, SP1 seemed to have a stronger effect on cements than SP2.

5.4.2 Rate of rebuilding of cement paste

Banfill and Saunders (1981) attributed the structural changes undergone by cement paste during shearing mode on two processes: induced shear and hydration. The latter is responsible for build-up of structure and, subsequently, yield stress development, whereas the former, for structure breakdown. It was therefore important to investigate how fast these cements recover their strength after shearing. The estimation of the rebuilding rate of cement pastes was done by defining the slope described by the variation of their thixotropy areas over time, as shown in Figure 5.12.

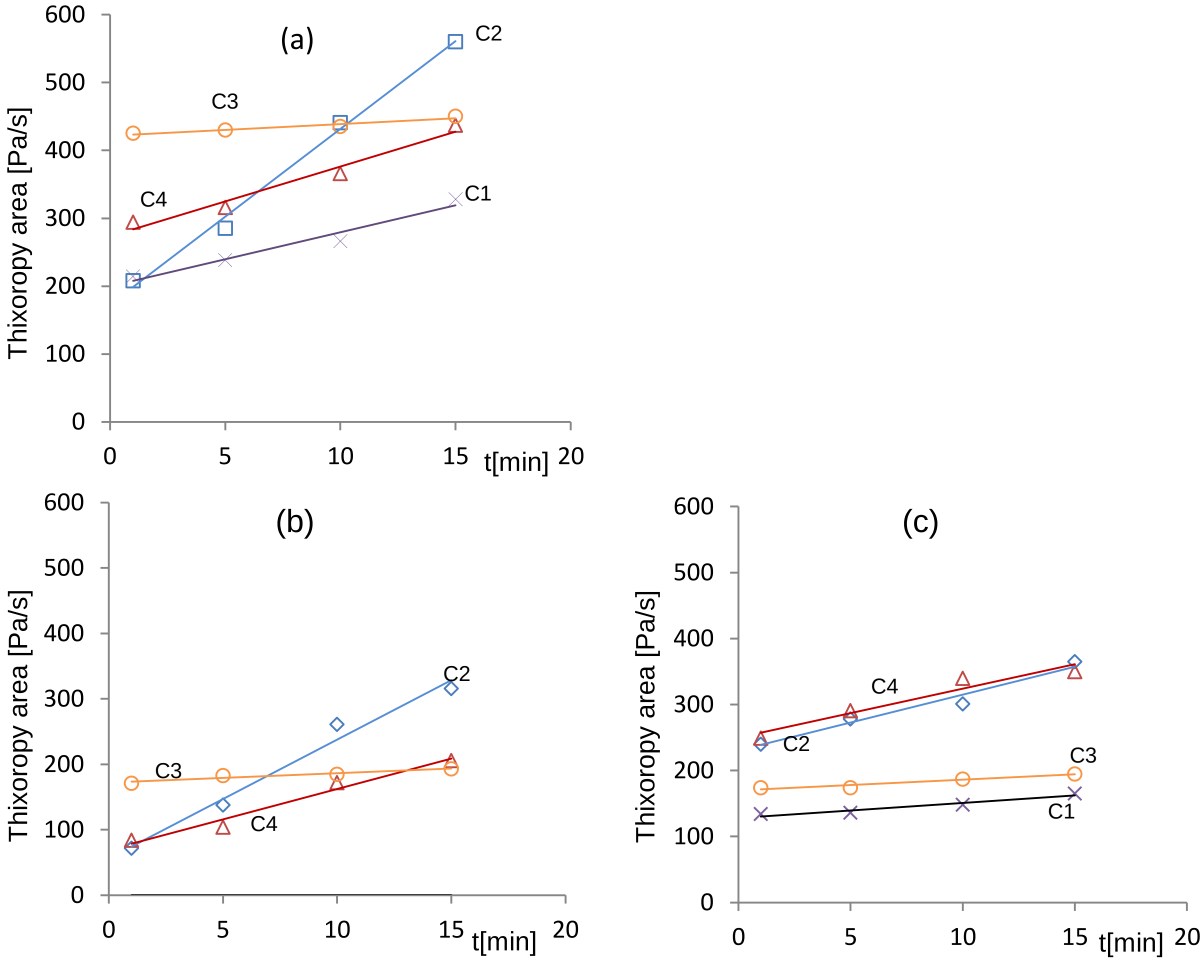


Figure 5.12: Rate of rebuilding of cement pastes: (a) without SP; (b) with SP1 (0.3%); and (c) with SP2 (0.3%)

Without SP in cements, Cements C2 and C4 had the highest rebuilding rates, while Cements C1 and C3 had the lowest rate of rebuilding. The introduction of SP in to the cement pastes decreased these rebuilding rates.

5.5 Effect of cement characteristics on rheology of cement paste

As discussed in the literature, the rheological behaviour of cement paste depends mostly on chemical and physical characteristics of cement. It was observed that the rheological characterisation of these cements, as determined by the different methods, followed the same trend, although each cement exhibited different values of yield stress depending on the method used. Subsequently, regardless of the characterisation method, in the absence of SP and presence of SP1, Cement C4 showed the highest values of yield stress followed by Cements C2, C3 and C1. In the presence of SP2, Cements C2 and C4 presented the highest yield stress values, while Cements C3 and C1 the lowest values.

Concering the viscosity of cement pastes, in the absence of SP, Cement C4 exhibited the highest values of plastic viscosity, followed by Cements C1, C2 and C3. In the presence of SP1, Cement C1 experienced the highest values, while Cement C3 the lowest. In the presence of SP2, Cements C1 and C2 exhibited the highest values of plastic viscosity, while Cements C3 and C4 the lowest.

5.5.1 Cement proprieties and cement paste yield stress value

Cement paste without SP

The difference in yield stress values of each cement was found to be affected mostly by the alkali content (Na_2O, K_2O) expressed in Na_2Oeq (alkali equivalent), obtained by calculating Na_2O + $0.658K_2O$ as reported by Mohammed and Asmaa (2010).

In the early hydration, high alkali content slowed down the yield stress development while the evolution of the same rheological parameter was found to be fast in cases where there was less alkali content in any given cement. Similar rheological behaviour was observed and reported by Mohammed and Asmaa (2010) during their investigation on the effect of alkali content on the micro-texture of cement paste. Pedrajas *et al.* (2014) reported the same behaviour and revealed the reason why the cement behaved in that manner: there are more hexagonal crystal portlandite precipitates in cement with low alkali equivalent, while in cement with high alkali content, more KOH and NaOH were generated, and as the hydration proceeded, these elements became more present in the liquid phase at increasing concentrations, raising the alkalinity and the pH of the cement paste favouring the repulsion effect between cement particles.

Therefore, Cement C4 with 0.33% of alkali equivalent content presented the fastest yield stress development, as could be seen in Figure 4.8. Cement C1 with high alkali equivalent content (0.75%) experienced the slowest yield stress development, followed by Cement C3 (0.29%) and

Cement C2 (0.41%). However, Cement C3 was supposed to have the fastest yield stress development because of its low alkali content, but due to the presence and high concentration of gypsum (2.92%) which was even greater than the C_3A content (1.84%), its hydration took longer and resulted in a slow yield stress development.

Plasticised cement paste

With the addition of SP, the competition between SO_3 and C_3A had a greater effect on the rheological parameters of cement. In fact, SO_3 reduces the ability of C_3A to absorb more SP on cement particles (Mukhopadhyay & Jang, 2009) and therefore, the balance between these two cement compounds is necessary in order to ensure a great adsorption of SP (Yamada *et al.,* 2001). In this study, it was noticed that cement in which there was an unbalanced concentration between SO_3 and C_3A (e.g. Cements C1 and C3) resulted in low yield stress values, whereas cement with moderated or balanced concentrations between these cement compounds (e.g. Cements C2 and C4) resulted in high yield stress values.

5.5.2 Cement properties and cement paste plastic viscosity value

Cement without SP

The plastic viscosity of cement pastes without SP was determined to be affected by the gypsum content in the cement.

As stated in section 2.3.5, in the early hydration during the C_3A phase, the cement stiffens or becomes more viscous quicker depending on the amount of gypsum in the cement. In fact, the presence of sulphate calcium during the first phase of hydration helps the cement paste remaining fluid for a while in order to avoid flash setting (Ghorab *et al.*, 2010).

It was found that cements with less gypsum content experienced a greater plastic viscosity evolution or were less fluid than cements with high gypsum content that exhibited lower plastic viscosity development and thus higher fluidity. According to Figure 4.9, Cement C4 with 1.29% of gypsum content had a high plastic viscosity evolution, followed by Cement C1 at 1.62%, Cement C2 at 2.74%, and Cement C3, which had the highest gypsum content at 2.92% experienced the lowest plastic viscosity growth.

Plasticised cement paste

The evolution of plastic viscosity of cement pastes in the presence of SP1 is presented in Figure 4.11. The difference in growth of plastic viscosity was caused by the alkali sulphate concentration in cements. Hanehara and Yamada (1999) demonstrated the effect of a few ion concentrations (such as SO_4^{2-}, Ca^{2+} o) on the early hydration of cement paste in the presence of different superplasticisers. When using polycarboxylate type SP, the fluidity of cement was reduced with the increase in soluble alkali sulphate (K_2SO_4).

Therefore, it was observed that cements with high K_2SO_4 content resulted in high plastic viscosity values, reducing the fluidity of cement. Similar behaviour was observed by Chandra and Björnströ (2002) and Ghorab *et al.* (2010). Cement C1 with 1.37% alkali sulphate experienced a low fluidity, while Cement C3 with low alkali sulphate concentration (0.31%) experienced the highest fluidity.

However, when using SP2, the fluidity of the paste seemed to be affected by the ion Ca^{2+} available in the C_3A hydration phase, as discussed by Pedrajas *et al.* (2014). High concentrations of these ions in the presence of polycarboxylate acid-based SP causes the cement to lose its fluidity due to the precipitation of considerable amount of hexagonal crystal portlandite during the first phase of hydration. It was observed that Cement C1 with 64% of CaO was the most viscous cement, while Cement C4 with 61.3% of CaO had the lowest plastic viscosity as compared to Cements C2 and C3, which had both 62.7% of CaO.

5.5.3 Cement properties and thixotropy of cement paste

When observing the thixotropic behaviour in terms of the cement rebuilding rate presented in Figure 5.12, it is remarkable that this rate could be directly related to the hydration products of cement pastes. It was found that cements with a high content of both alkali sodium and C_3A experienced a high rate of structural rebuilding. Quanji (2010) reported similar behaviour, explaining that when cement comes in contact with water, Ca^{+2} and OH^- ions are released, combining to aid the quick dissolution of alkali, especially sodium, and resulting in stronger attractive forces and more cohesive paste. Mewis and Wagner (2009) stated that the presence of some salts in cement pastes increases the attractive forces between particles. Consequently, cements with high C_3A and high Na_2O such as Cement C1 (3.95%, 0.34%) and Cement C2 (2.75%, 0.19%) performed a greater rate of rebuilding than Cement C3 (1.84%, 0.15%) and Cement C4 (2.63%, 0.18%) that had lower concentrations of these elements.

Particular attention should be given to the cubic crystal formation (cC_3A) that is more active than the orthorhombic formation of C_3A (Quanji, 2010; Vikan *et al.*, 2007). Cement C2, with more cC_3A content (0.16%), restructured faster than Cement C1, which had a high total C_3A content but with less cC_3A (0.13%) in its phase.

Similarly, Cement C4 restructured faster than Cement C3 due to the difference in K_2SO_4 (salt) that was higher in Cement C4 (1,34%) than Cement C3 (0.331%). The effects of attractive forces were therefore more pronounced in Cement C4 than in Cement C3, as reported previously by Mewis and Wagner (2009).

It is worth noting that with the addition of SP, the rate of rebuilding of cement pastes was reduced due to the presence of repulsive forces between particles according to the cement characteristics as described in section 2.3.6. Finally, for a great rebuilding rate of cement paste, a suitable balance between C_3A (particularly its cC_3A formation), alkali (especially Na_2O) and the amount of salt (K_2SO_4) in cement is required.

5.6 Conclusion

The main purpose of this work was to determine the effect of cement characteristics and their compatibility with two types of SPs on the rheological behaviour of cement paste. Results pertaining to flow properties of cement pastes in the presence and absence of SP were discussed in this chapter. Yield stress values determined from the conventional flow curve, construction of flow curve and amplitude sweep were reported and compared. Yield stress values from conventional flow curve did not indicate any change in the microstructure of cement paste. Those from construction of flow curve depicted the evolution of cement paste structure and were similar to the yield stress values as determined by amplitude sweep.

The effects of SPs on the rheological parameters – including yield stress development, plastic viscosity evolution and thixotropy behaviour of cement pastes – were also considered. The addition of SP in cement paste decreases the yield stress values, the viscosity values, the rate of rebuilding and the hydration rate.

The equation of self-acceleration type was developed to predict the kinetics of cement paste hydration. There was a relationship between the peak time of cement paste G'' and T^* the constant of the model that described the time at which the storage modulus reaches the plateau during hydration.

These observed rheological behaviours are linked to the chemical and mineralogy composition of cements.

Chapter 6 Conclusions and recommendation

The promotion of self-compacting concrete in the South Africa construction industry requires that the effect of the local cement and their interactions with commercial admixtures be determined and understood thoroughly. To this end, four different cements of the same type 52.5N produced by one local company at different factories, and two types of superplasticisers, were investigated at paste scale to study the effects of their characteristics on both flow and elastic properties of self-compacting cement paste. This chapter presents a general summary of the work conducted with regards to the findings of the investigation, followed by recommendations for future research.

6.1 Yield stress and plastic viscosity of cement paste

Yield stresses of cement pastes were measured in two different modes using three different techniques, including two existing methods: 1) the conventional flow curve (shearing mode) and 2) the amplitude sweep (dynamic or oscillatory mode). As these measuring methods are ineffective, a third technique was required: 3) obtaining rheological parameters by constructing the flow curves.

This research showed the inadequacy of the conventional flow curve: firstly, the material was continuously destroyed and no relevant information pertaining to the microstructure of cement paste could be obtained. Even after a long period of resting time, the pre-shearing was found to be enough to destroy the formed structure, giving yield stress values that were not different from early resting times; secondly, the use of rheological models to help obtain the stress at zero shear rate does not take into consideration the time dependency of cement paste.

With the constitutive equations, it is assumed that the viscosity of the material is constant over time and corresponds to the viscosity value of a Newtonian material that would behave in the same way as a non-Newtonian fluid at that particular shear rate. Cement pastes are ‘living’ systems with continuously changing structure, and consequently, their rheological properties, a single value of viscosity at specific shear rates, had to be determined for using these models rationally.

On the other hand, the evaluation of yield stress by amplitude sweep, although a non-destructive technique, could only provide a single value of yield stress. This method also does not give any details about the microstructure evolution of cement paste since the stresses before the critical stress (yield stress) are independent of the storage modulus, and when this value is exceeded, the structure of the material is destroyed.

The instantaneous values of yield stress and plastic viscosity of cement paste could only be obtained by constructing flow curves. A quantitative evaluation of cement paste workability was rendered by monitoring the growth of these rheological parameters.

Finally, the yield stress values as provided by each of these three techniques were compared, and the following was concluded:

- The yield stress obtained by constructing the flow curve is the *only* method which gives information about the evolution of the rheological properties, reflecting structure evolution of cements pastes.

- The yield stress values of cement paste as determined by amplitude sweep are always higher as compared to the two other methods due to the fact that during experiments the hydration is not disturbed and the microstructure is not destroyed.

- The yield stress values obtained from constructing the flow curves are close to those evaluated by the amplitude sweep method.

- Yield stress values determined by hysteresis loops appear to be low as compared to the values obtained by the two other techniques. This might be explained by the fact that during the experiments, the structure of the material is continuously destroyed from shearing. The pre-shearing at 50 s^{-1} for less than 15 s is sufficient to destroy the cement paste structure formed even after 15 minutes.

Regardless of which technique was used, it was possible to depict the effect of cement-SP interactions on the rheological behaviour of cement pastes. Subsequently, in the absence of SP, the concentration of alkali equivalent in cements was found to be the cause of cement paste yield stress fluctuations, while the fluidity of cement paste was controlled by the gypsum content. However, with plasticised cement pastes, the balance between the concentration of C_3A and SO_3 in cements governed the differences observed in their yield stress values, whereas the variations in plastic viscosity values were found to be caused by the alkali sulphate K_2SO_4 and CaO contents, depending on the SP used.

6.2 Rheokinetics of cement paste

A new method has been proposed to follow the kinetics of hydration for cementitious materials, one which consists of measuring the time dependence of the elastic modulus in the linear viscoelastic domain and fitting of experimental data by the kinetic equation of self-acceleration type. This model provides two constants (i.e. the characteristic time that defines the initial rate of hydration process and the self-acceleration coefficients).

It was determined that this model predicts the kinetics of hydration well. Consequently, the effect of cement characteristics and the efficiency of SPs used on the cement paste microstructure could be determined.

Flow properties of cement pastes could be related to the constants of the model and were in good agreement with the literature.

Cements with higher characteristic times and self-acceleration constant values experienced a low rate of hydration resulting in a slow modulus growth, whereas cements with lower values of these constants experienced a rapid stress growth due to a high rate of hydration.

6.3 Thixotropic behaviour of cement paste

The thixotropy areas of cement pastes increased as the resting time was prolonged, likely due to the effect of hydration on the development of internal forces between cement paste particles; however, these areas decreased with the introduction of SP in the cement paste.

The rates of rebuilding of unplasticised cements were higher than those of plasticised cement pastes. These rates depended on the yield stress development of each cement. Cements with higher yield stress development had a higher rate of rebuilding, while those with lower yield stress growth resulted in lower rebuilding rates.

The thixotropy behaviour of cement pastes were strongly influenced by the hydration products including the C_3A, particlularly its cubic formation, and both the alkali sodium and sulfate contents in cement.

6.4 Significant contribution

Finally, the current investigation would aid manufacturers to improve and control the quality of their cement in order to produce a concrete with desired flow properties. In other words, flow properties of concrete can be controlled beforehand at industrial levels.The findings of this study also make possible the minimising or eradicating of problems related to concrete during pumping, placement and formwork lateral pressure.

Mostly, the research contributed a new technique in rheometry of time-dependent materials to make the evaluation of their rheological parameters more rational. The mechanism of cement paste hydration is well-understood and can now be predicted.

The findings of this work have been published in Applied Rheology Journal:
Mbasha W, Masalova I, Haldenwang R and Malkin A. 2015. *The yield stress of cement pastes as obtained by different rheological approaches*. Applied Rheology. DOI: 10.3933/ApplRheol-25-53517

6.5 Recommendation or further research

This study focused on the rheological behaviour of cement pastes with and without SP. Further research on the rheological behaviour of cement paste with mineral extenders such as fly ash and slag could be considered for determining the effect of these extenders on flow properties of SCC. Also the effectiveness of the rheokinetic model to various cementitious materials could be evaluated. In addition, since the effect of cement characteristics on the flow behaviour of self-compacting cement paste have been determined, a quantitative analysis of the chemical compositions of cement could be done in order to see whether it woud be possible to control the flow behaviour of SCCP.

References

Agarwal, S., Masood, I. & Malhotra, S. 2000. Compatibility of superplasticizers with different cements. *Construction and Building Materials*, 14: 253–259.

Aiqin, W., Chengzhi, Z. & Ningsheng, Z. 1997. Study of the influence of the particle size distribution on the properties of cement. *Cement and Concrete Research*, 27(5): 685–695.

Asaga, K. & Roy, D. 1980. Rheological properties of cement mixes: effects of superplasticizers on viscosity and yield stress. *Cement and Concrete Research*, 10(2): 287–295.

Assaad, J.J., Harb, J. & Maalouf, Y. 2014. Measurement of yield stress of cement pastes using the direct shear test. *Journal of Non-Newtonian Fluid Mechanics*, 214: 18–27.

Autier, C., Azéma, N. & Boustingorry, P. 2014. Using settling behaviour to study mesostructural organization of cement pastes and superplasticizer efficiency. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 450: 36–45.

Banfill, P.F.G. 2006. Rheology of fresh cement and concrete. *Rheology reviews*, 2006: 61.

Banfill, P.F.G. 2003. The rheology of fresh cement and concrete-a review. In *11th International Cement chemistry congres*. Durban.

Banfill, P.F.G. & Saunders, D. 1981. On the viscometer examination of cement pastes. *Cement and Concrete Research*, 11: 363–370.

Barnes, H.A., Hutton, J.F. & Walters, K. 1989. *An introduction to rheology*. Elsevier.

Beaupré, D., Chapdelaine, F., Domone, P., Koehler, E., Shen, L., Sonebi, M., Struble, L., Tepke, D., Wallevik, J.E. & Wallevik, O. 2004. Comparison of concrete rheometers: International tests at MBT (Cleveland OH, USA) in May 2003.

Bellotto, M. 2013. Cement paste prior to setting: A rheological approach. *Cement and Concrete Research*, 52: 161–168.

Bhatty, J. 1987. The effect of retarding admixtures on the structural development of continuously sheared cement pastes. *The International Journal of Cement Composite and Lightweight Concrete*, 9(3).

Bishnoi, S. 2008. *Vector modelling of hydrating cement microstructure and kinetics*. Citeseer.

Bishnoi, S. & Scrivener, K.L. 2009. Studying nucleation and growth kinetics of alite hydration using μic. *Cement and Concrete Research*, 39(10): 849–860.

Celik, I.B. 2009. The effects of particle size distribution and surface area upon cement strength development. *Powder Technology*, 188(3): 272–276.

Chandra, S. & Björnström, J. 2002. Influence of cement and superplasticizers type and dosage on the fluidity of cement mortars - Part I. *Cement and Concrete Research*, 32(10): 1605–1611.

Chhabra, R.P. & Richardson, J.F. 1999. *Non-Newtonian flow in the process industries*. Butterworth-Heinemann Oxford.

Chow, T., McIntire, K.R.K. & Cooke, C. 1988. The rheological properties of cement slurries: effect of vibration, hydration conditions, and additives. *SPE Production Engineering*, 3(4): 543–550.

Diamantonis, N., Marinos, I., Katsiotis, M.S., Sakellariou, A., Papathanasiou, A., Kaloidas, V. & Katsioti, M. 2010. Investigations about the influence of fine additives on the viscosity of cement paste for self-compacting concrete. Construction and Building Materials, 24(8): 1518–1522.

Eirich, F.R. 1956. *Theory and Applications*. Academic Press.

El Barrak, M., Mouret, M. & Bascoul, A. 2009. Self-compacting concrete paste constituents: Hierarchical classification of their influence on flow properties of the paste. *Cement and Concrete Composites*, 31(1): 12–21.

Esping, O. 2007. *Early age properties of self-compacting concrete-Effects of fine aggregate and limestone filler*. Chalmers University of Technology,

Ferguson, J. & Kemblowski, Z. 1991. *Applied fluid rheology*. Springer Netherlands.

Fernàndez-Altable, V. & Casanova, I. 2006. Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures. *Cement and Concrete Research*, 36(7): 1222–1230.

Ferraris, C.F., Obla, K.H. & Hill, R. 2001. The influence of mineral admixtures on the rheology of cement paste and concrete. *Cement and Concrete Research*, 31(2): 245–255.

Garrault, S., Behr, T. & Nonat, A. 2006. Formation of the C−S−H Layer during Early Hydration of Tricalcium Silicate Grains with Different Sizes. *The Journal of Physical Chemistry B*, 110(1): 270–275.

Geel, A., Beushausen, H. & Alexander, M. 2007. SCC in South Africa - The challenge to introduce a new technology to the constrcution industry. In *5th International RILEM symposium on self-compacting concrete*. Self-compacting concrete. RILEM Publications: 1035–1040.

Geiker, M.R., Brandl, M., Thrane, L.N., Bager, D.H. & Wallevik, O. 2002. The effect of measuring procedure on the apparent rheological properties of self-compacting concrete. *Cement and Concrete Research*, 32(11): 1791–1795.

Ghorab, H.Y., Antar, A. & Taha, M.A.N. 2010. The C3A-gypsum system in alkali sulfate solutions. *Ceramics-Silikáty*, 54(1): 53–59.

Golaszewski, J. 2008. Influence of cement properties on rheology of fresh cement mortars without and with superplasticizer. *Arch Civil Eng Environ–ACEE*, 4.

Hackley, V.A. & Ferraris, C.F. 2001. *Guide to Rheological Nomenclature: Measurements in Ceramic Particulate Systems*. United States Department of Commerce, Technology Administration, National Institute of Standards and Technology.

Haldenwang, R. & Fester, V. 2013. Effect of superplasticisers on the reproducibility of self-compacting concrete. *SCC seminar*.

Hall, C. 2009. Cement and concrete material: materials fundamentals + mix design.

Hanehara, S. & Yamada, K. 1999. Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology. *Cement and Concrete Research*, 29(8): 1159–1165.

Hildago, J., Struble, L., Leslies, J. & C.T.C. 2008. Correlation between paste and concrete flow behaviour. *Material Journal*, 105: 281–288.

Hommer, H. & von Seyerl, J. 2008. Impact of Dispersant Structure on Workability and Green Strength Development of LCC at Different Temperatures. In *51th International colloquium on refractories*. Aachen, Germany: 92–94.

http://www.engineeringintro.com/uncategorized/cement-manufacturing-process

Jang, S.H. 2009. *Identification of concrete incompatibilities using cement paste rheology*. Texas A&M University.

Jarny, S., Roussel, N., Le Roy, R. & Coussot, P. 2008. Modelling thixotropic behaviour of fresh cement pastes from MRI measurements. *Cement and Concrete Research*, 38(5): 616–623.

Justnes, H. & Vikan, H. 2005. Viscosity of cement slurries as a function of solids content. *Ann. Trans. Nordic Rheology Soc*, 13: 75–82.

Khayat, K.H., Omran, A.F. & Al Magdi, W. 2012. Evaluation of thixotropy of self-consolidating concrete and influence on concrete performance. In *Proceedings 3rd Iberian Congress on Self Compacting Concrete, Madrid*. 3–16.

Kim, B.G., Jiang, S., Jolicoeur, C. & Aitcin, P.C. 2000. The adsorption behaviour of PNS superplasticizer and its relation to fluidity of cement paste. *Cement and Concrete Research*, 30: 887–893.

Kirby, G.H. & Lewis, J.A. 2004. Comb polymer architecture effects on the rheological property evolution of concentrated cement suspensions. *Journal of the American Ceramic Society*, 87(9): 1643–1652.

Koehler, E.P. 2007. *Aggregates in self-compacting concrete*. Ph Doctorate. Austin: University of Texas.

Krieger, I.M. & Dougherty, T.J. 1959. A mechanism for non-Newtonian flow in suspensions of rigid spheres. *Transactions of the Society of Rheology (1957-1977)*, 3(1): 137–152.

Kurtis, K. portland cement hydration.

Lapasin, R., Longo, V. & Rajgelj, S. 1979. Thixotropic behaviour of cement paste. *Cement and Concrete Research*, 9: 309–318.

Lapasin, R., Papo, A. & Rahgelj, S. 1983. Flow behaviour of fresh cement pastes. A comparison of different rheological instruments and technique. *Cement and Concrete Research*, 13: 349–356.

Libre, N.A., Khoshnazar, R. & Shekarchi, M. 2010. Relationship between fluidity and stability of self-consolidating mortar incorporating chemical and mineral admixtures. *Construction and Building Materials*, 24(7): 1262–1271.

Lootens, D., Jousset, P., Martinie, L., Roussel, N. & Flatt, R.J. 2009. Yield stress during setting of cement pastes from penetration tests. *Cement and Concrete Research*, 39(5): 401–408.

López, A., Tobes, J.M., Giaccio, G. & Zerbino, R. 2009. Advantages of mortar-based design for coloured self-compacting concrete. *Cement and Concrete Composites*, 31(10): 754–761.

Malkin, A.Y. & Kulichikhin, S. *Rheokinetics: rheological transformations in synthesis and reactions of oligomers and polymers*.

Mewis, J. & Wagner, N.J. 2009. Thixotropy. *Advances in Colloid and Interface Science*, 147-148: 214–227.

Mikanovic, N. & Jolicoeur, C. 2008. Influence of superplasticizers on the rheology and stability of limestone and cement pastes. *Cement and Concrete Research*, 38(7): 907–919.

Min, B., Jennings, H.M. & Erwin, L. 1993. Hysteresis loops of cement paste measured by oscillatory shear experiments. *Korean Journal of Rheology*, 5(2): 99–108.

Mohammed, M.S. & Asmaa, M.A. 2010. The Effect of Alkalis on The Properties of Portland Cement.

Moore, C. 1982. Chemical control of Portland cement clinker. *Ceramic Bulletin*: 511–515.

Mukhopadhyay, A.K. & Jang, S. 2009. *Using Cement Paste Rheology to Predict Concrete Mix Design Problems: Technical Report*. Texas Transportation Institute, Texas A&M University System.

Nachbaur, L., Mutin, J. & Choplin, L. 2001. dynamic mode rheology of cement and tricalcium silicate paste from mixing to setting. *Cement and Concrete Research*, 31: 183–192.

Nehdi, M. & Al Martini, S. 2009. Estimating time and temperature dependent yield stress of cement paste using oscillatory rheology and genetic algorithms. *Cement and Concrete Research*, 39(11): 1007–1016.

Nehdi, M. & Rahman, M.A. 2004. Estimating rheological properties of cement pastes using various rheological models for different test geometry, gap and surface friction. *Cement and Concrete Research*, 34(11): 1993–2007.

Nelson, E.B., Baret, J.F. & Michaux, M. 1990. 3 Cement Additives and Mechanisms of Action. *Elsevier*, 28: 3–37.

Neophytou, M.K.A., Pourgouri, S., Kanellopoulos, A.D., Petrou, M.F., Loannou, L., Georgiou, G. & Alexandrou, A. 2010. Determination of the rheological parameters of self-compacting concrete matrix using slump flow test. *Applied Rheology*, 20: 62402–1 – 62402–20.

Nunes, S., Oliveira, P.M., Coutinho, J.S. & Figueiras, J. 2011. Rheological characterization of SCC mortars and pastes with changes induced by cement delivery. *Cement and Concrete Composites*, 33(1): 103–115.

Okamura, H. & Ouchi, M. 2003. Applications of self-compacting concrete in Japan. In *3rd International RILEM symposium*. Self-compacting concrete. Reykjavik, Iceland: RILEM Publications: 3–5.

De Oliviera, L.A.P., Gomes, J.P.C. & Nepomuceno, M.C.. 2013. The influence of waste materials on the rheology of rendering mortars. *Applied Rheology*, 23(1): 37–47.

Otsubo, Y., Miyai, S. & Umeya, K. 1980. Time-dependent flow of cement pastes. *Cement and Concrete Research*, 10(5): 631–638.

Pedrajas, C., Rahhal, V. & Talero, R. 2014. Determination of characteristic rheological parameters in Portland cement pastes. *Construction and Building Materials*, 51: 484–491.

Puertas, F., Santos, H., Palacios, M. & Martínez-Ramírez, S. 2005. Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes. *Advances in Cement Research*, 17(2): 77–89.

Quanji, Z. 2010. *Thixotropic behaviour of cement-based materials - effect of clay and cement types.* Master of Science. Iowa: Iowa State University.

Rahman, M.K., Baluch, M.H. & Malik, M.A. 2014. Thixotropic behaviour of self compacting concrete with different mineral admixtures. *Construction and Building Materials*, 50: 710–717.

Ran, Q., Somasundaran, P., Miao, C., Liu, J., Wu, S. & Shen, J. 2009. Effect of the length of the side chains of comb-like copolymer dispersants on dispersion and rheological properties of concentrated cement suspensions. *Journal of Colloid and Interface Science*, 336(2): 624–633.

Roussel, N. 2005. Steady and transient flow behaviour of fresh cement pastes. *Cement and Concrete Research*, 35(9): 1656–1664.

Roussel, N., Ovarlez, G., Garrault, S. & Brumaud, C. 2012. The origins of thixotropy of fresh cement pastes. *Cement and Concrete Research*, 42(1): 148–157.

Roy, D. & Asaga, K. 1979. Rheological properties of cement mixes: iii. the effects of mixing procedures on viscometric properties of mixes containing superplasticizers. *Cement and Concrete Research*, 9: 731–739.

Sant, G., Ferraris, C.F. & Weiss, J. 2008. Rheological properties of cement pastes: A discussion of structure formation and mechanical property development. *Cement and Concrete Research*, 38(11): 1286–1296.

Schultz, M. & Struble, L.J. 1992. Use of oscillatory shear to study flow behaviour of fresh cement paste. *Cement and Concrete Research*, 23(2): 273–282.

Schwartzentruber, L.D., Le Roy, R. & Cordin, J. 2006. Rheological behaviour of fresh cement pastes formulated from a self-Compacting Concrete (SCC). *Cement and Concrete Research*, 36(7): 1203–1213.

Sheinn, A.M.M. 2007. *Rheological modelling of self-compacting concrete*. Ph Doctorate. National University of Singapore.

Shi, C., Wu, Z., Lv, K. & Wu, L. 2015. A review on mixture design methods for self-compacting concrete. *Construction and Building Materials*, 84: 387–398.

Struble, L.J. & Leit, W. 1995. Rheological changes associated with setting of cement paste. *Advanced Cement Based Materials*, 2(6): 224–230.

Struble, L.J. & Wei-Guo, L. 1995. rheological change associated with setting time. *Advanced Cement Based Materials*, 2(6): 224–230.

Swan, C. Portland cement concrete.

Tattersall, G.H. & Banfill, P.F.G. 1983. *Rheology of Fresh Concrete*. London: Pitman Advanced Publishing Program.

Vikan, H. 2005. *Rheology and reactivity of cementitious binders with plasticizers*. Ph Doctorate. Trondheim: Norwegian University of Science and Technology.

Vikan, H., Justnes, H., Winnefeld, F. & Figi, R. 2007. Correlating cement characteristics with rheology of paste. *Cement and Concrete Research*, 37(11): 1502–1511.

Wallevik, J.E. 2005. Thixotropic investigation on cement paste: Experimental and numerical approach. *Journal of Non-Newtonian Fluid Mechanics*, 132(1-3): 86–99.

Wallevik, O. 2003. Rheology-A scientific approach to develop self-compacting concrete. In *3rd International RILEM symposium*. Self compacting concrete. Reykjavik, Iceland: RILEM Publications: 23–30.

Walraven, J. 2003. Structural aspects of self compacting concrete. In *3rd International RILEM symposium*. Self-compacting concrete. Reykjavik, Iceland: RILEM Publications: 15–22.

Whorlow, R. 1992. *Rheological techniques*. 2, Illustrated. University of Michigan: Ellis Horwood Limited.

Williams, D.A., Saak, A.W. & Jennings, H.M. 1999. The influence of mixing on the rheology of fresh cement paste. *Cement and Concrete Research*, 29(9): 1491–1496.

Yamada, K., Ogawa, S. & Hanehara, S. 2001. Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase. *Cement and Concrete Research*, 31(3): 375–383.

Yang, M. & Jennings, H.M. 1995. Influences of mixing methods on the microstructure and rheological behaviour of cement paste. *Advanced Cement Based Materials*, 2(2): 70–78.

Zhang, M.H., Ferraris, C.F., Zhu, H., Picandet, V., Peltz, M.A., Stutzman, P. & De Kee, D. 2010. Measurement of yield stress for concentrated suspensions using a plate device. *Materials and Structures*, 43(1-2): 47–62.

Zhan, Y. & Napier-Munn, T. 1995. Effects of particle size distribution, surface composition on Portland cement. *Powder Technology*, 83: 245–252.

Zingg, A., Winnefeld, F., Holzer, L., Pakusch, J., Becker, S., Figi, R. & Gauckler, L. 2009. Interaction of polycarboxylate-based superplasticizers with cements containing different C_3A amounts. *Cement and Concrete Composites*, 31(3): 153–162.

Appendices

Appendix A. Optimisation of superplasticisers dosage

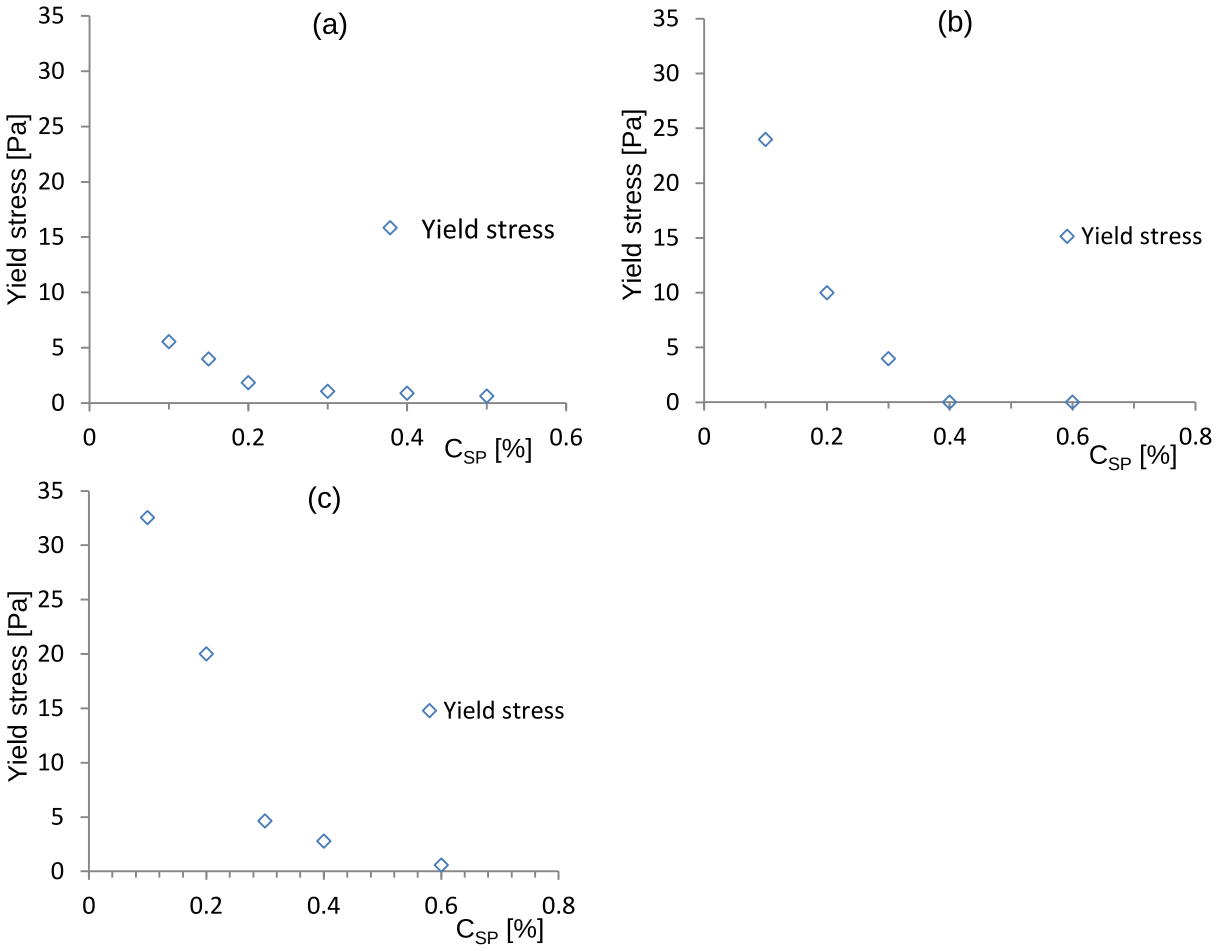


Figure A.1: Yield stress change over SP1 for: (a) Cement C1; (b) Cement C3; and (c) Cement C4

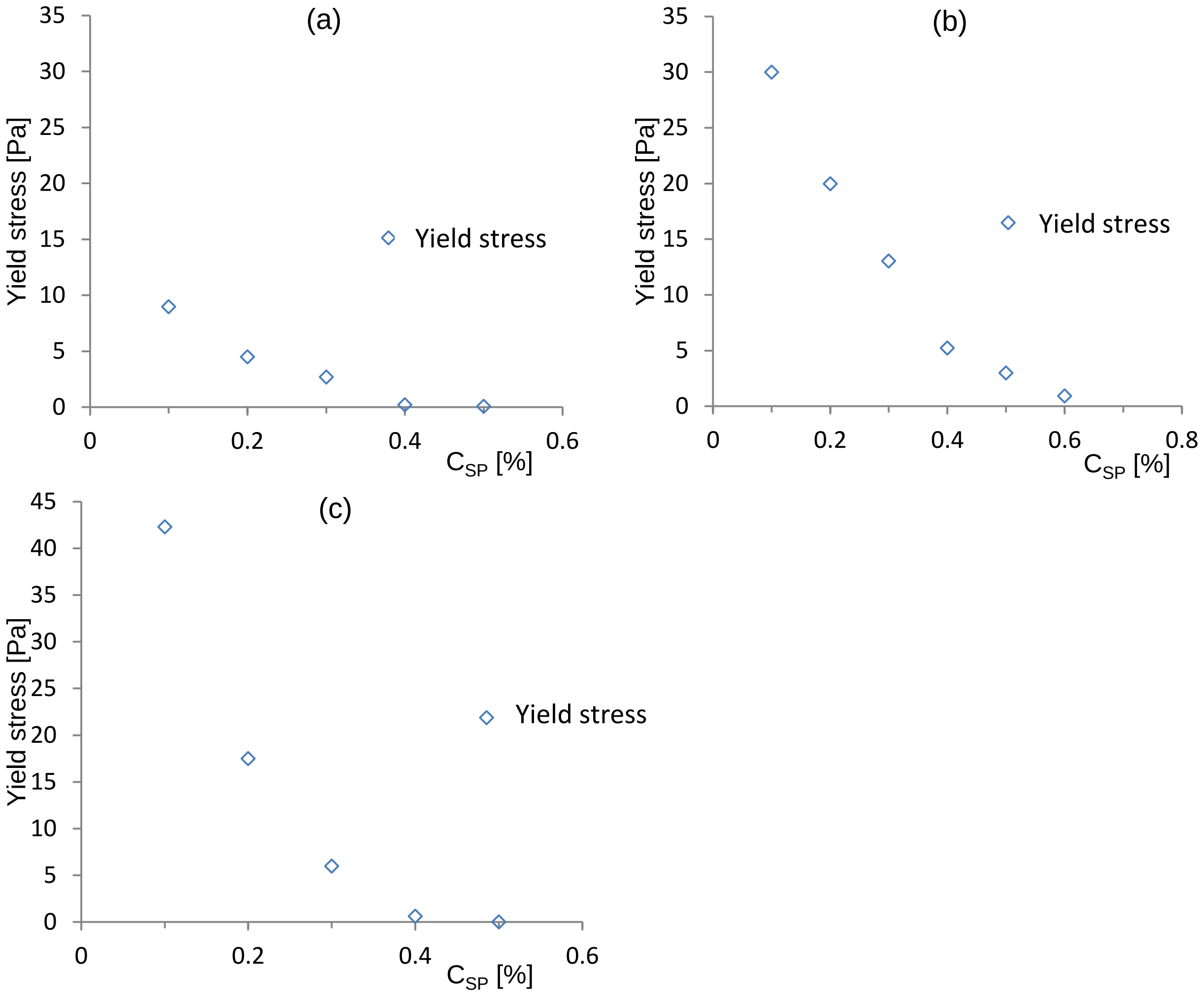


Figure A.2: Yield stress change over SP2 for: (a) Cement C1; (b) Cement C3; and (c) Cement C4

Appendix B. Flow curves at different times for all cements with SP

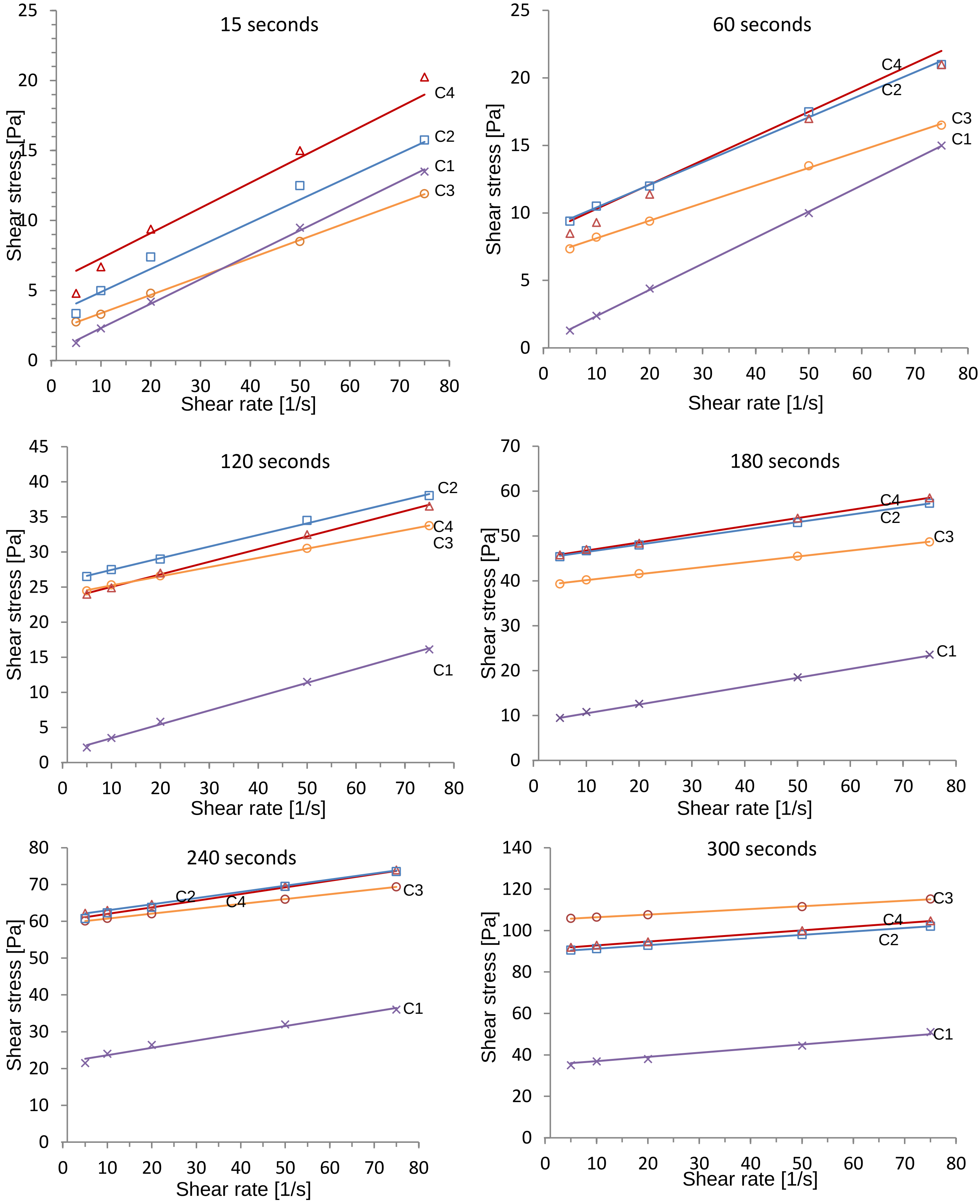
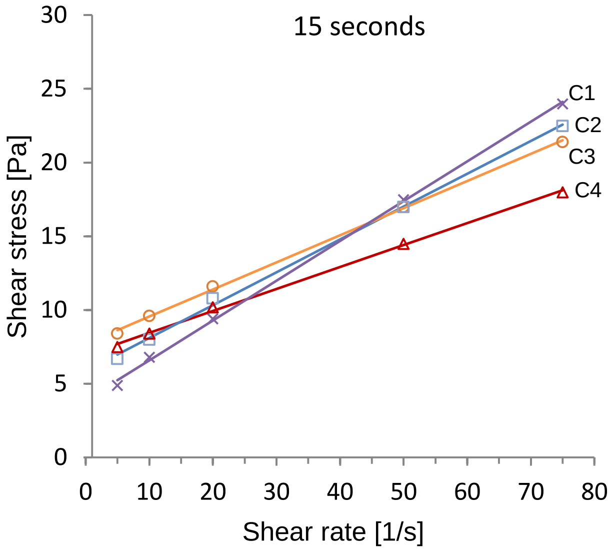
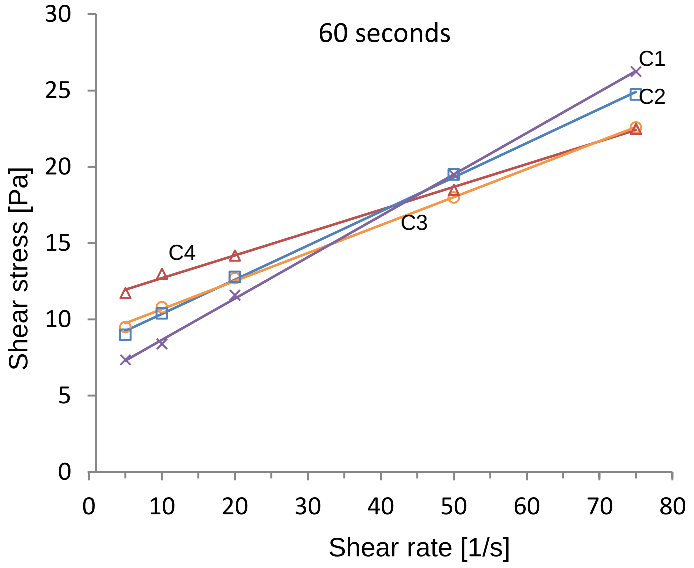
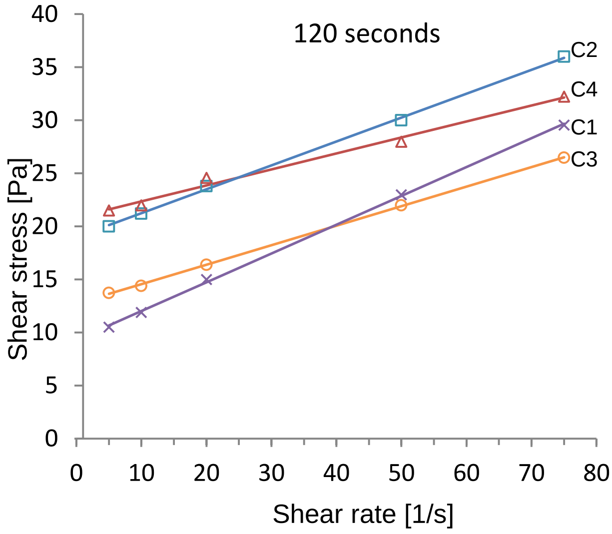
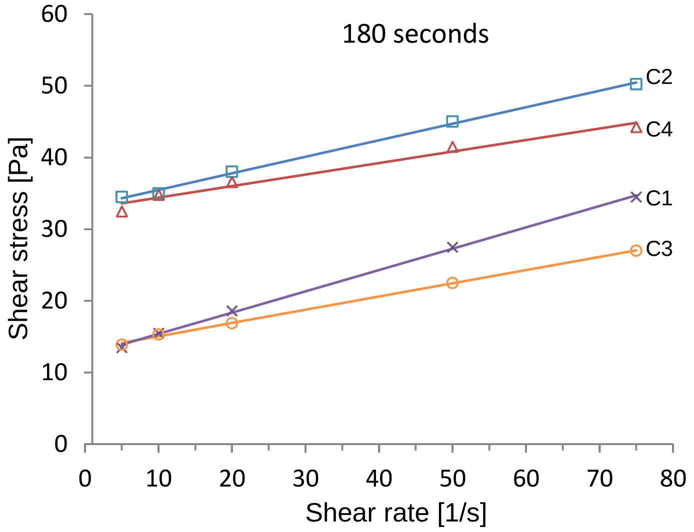


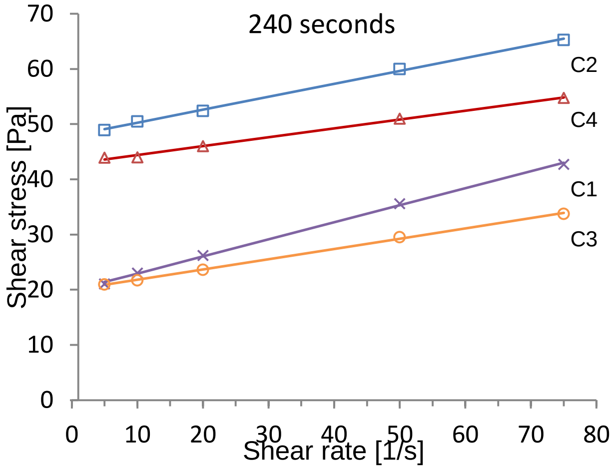
Figure B.1: Flow curves at different times of all cements with SP1

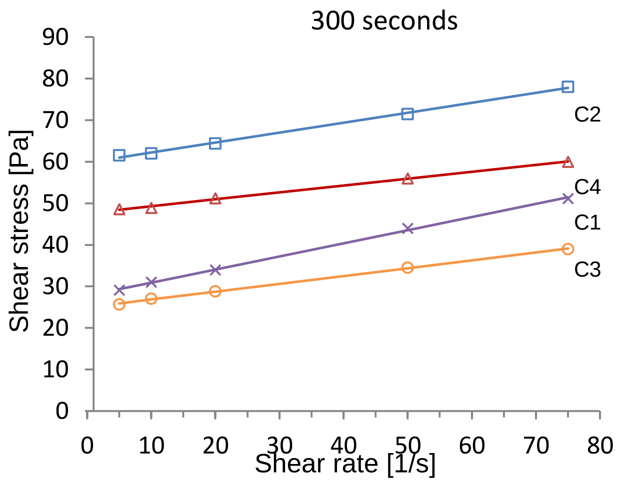

15 seconds
Shear stress [Pa]
Shear rate [1/s]
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70
80
C1
C2
C3
C4


60 seconds
Shear stress [Pa]
Shear rate [1/s]
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70
80
C1
C2
C4
C3


120 seconds
Shear stress [Pa]
Shear rate [1/s]
0
5
10
15
20
25
30
35
40
0
10
20
30
40
50
60
70
80
C2
C4
C1
C3


180 seconds
Shear stress [Pa]
Shear rate [1/s]
0
10
20
30
40
50
60
0
10
20
30
40
50
60
70
80
C2
C4
C1
C3


240 seconds
Shear stress [Pa]
Shear rate [1/s]
0
10
20
30
40
50
60
70
0
10
20
30
40
50
60
70
80
C2
C4
C1
C3


300 seconds
Shear stress [Pa]
Shear rate [1/s]
0
10
20
30
40
50
60
70
80
90
0
10
20
30
40
50
60
70
80
C2
C4
C1
C3

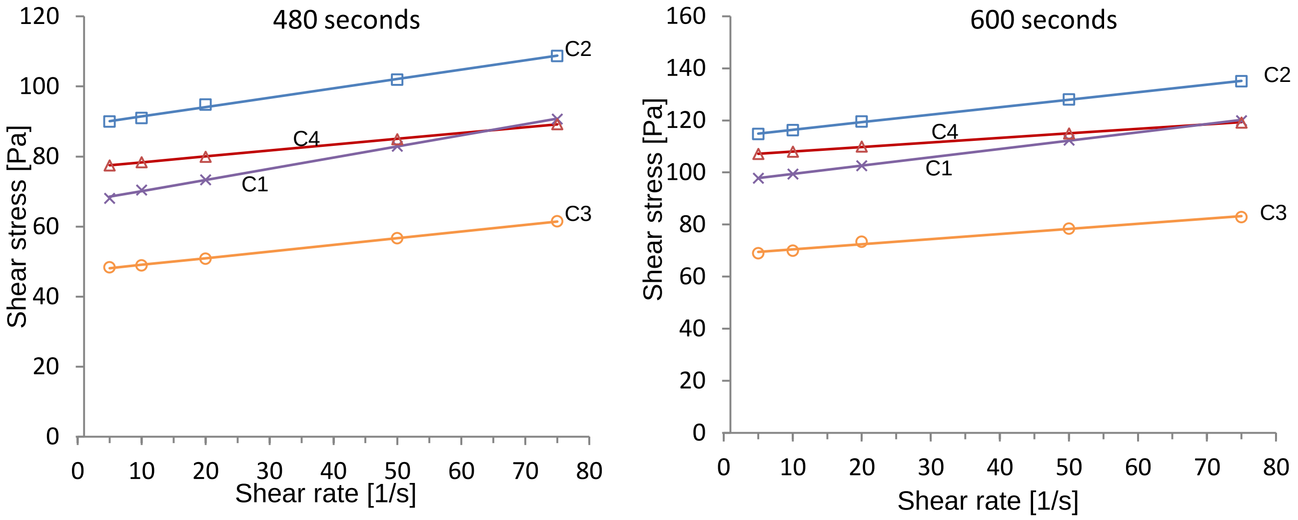


Figure B.2: Flow curves at different times of all cements with SP2

Appendix C. Hysteresis loops of cements without SP

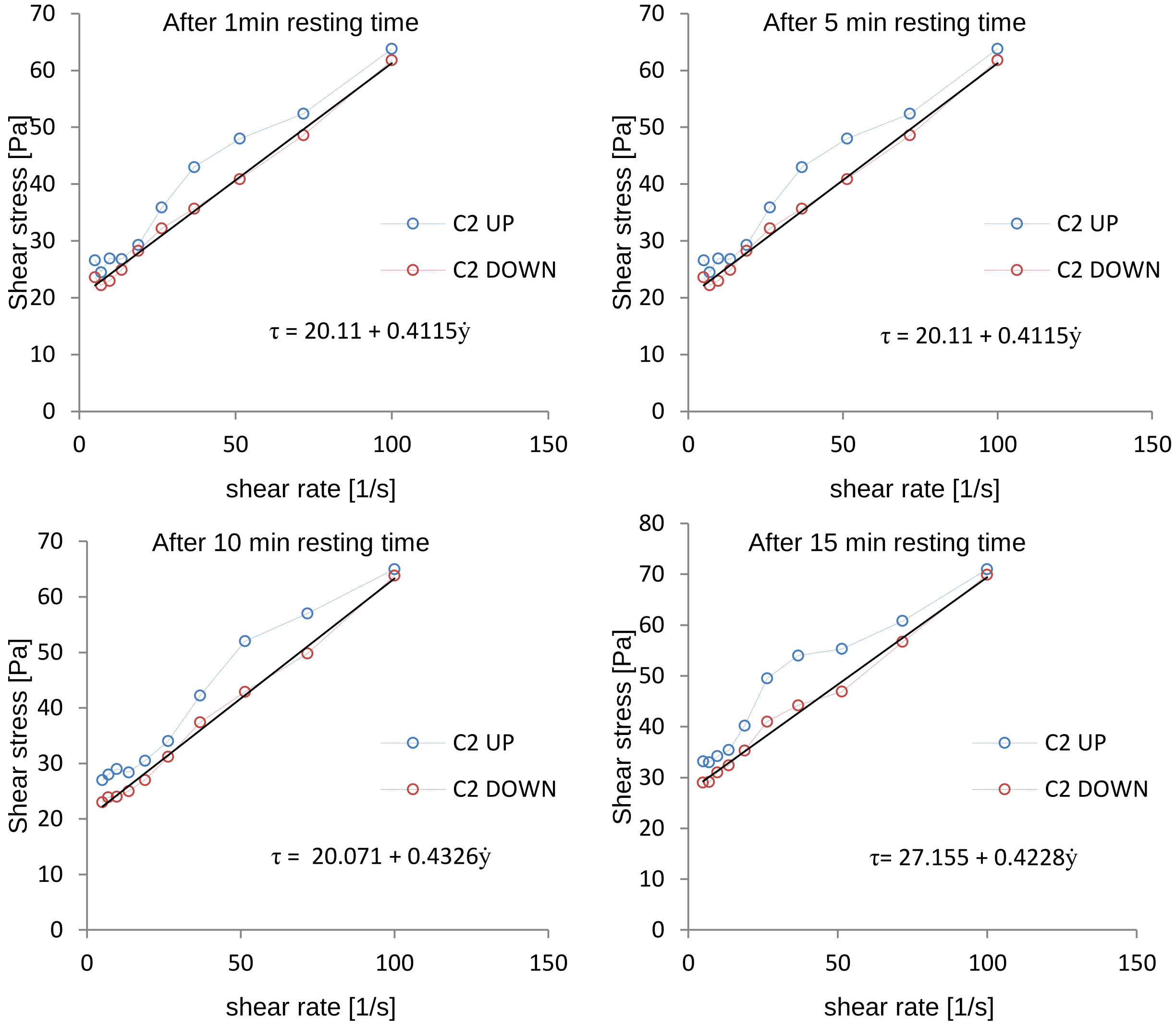


Figure C.1: Rheological parameters from hysteresis loop after different times for Cement C2 with no SP

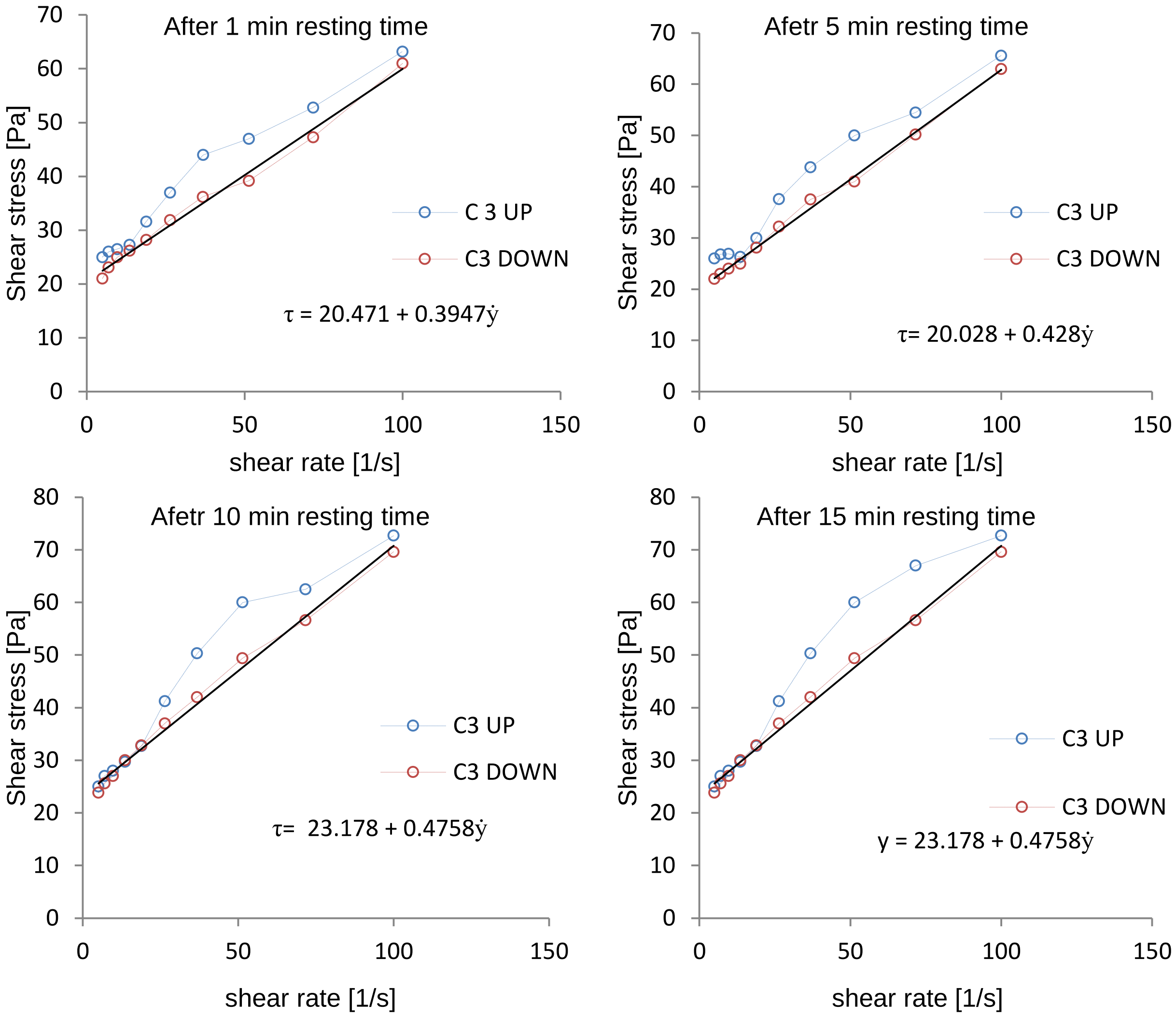


Figure C.2: Rheological parameters from hysteresis loop after different times for Cement C3 with no SP

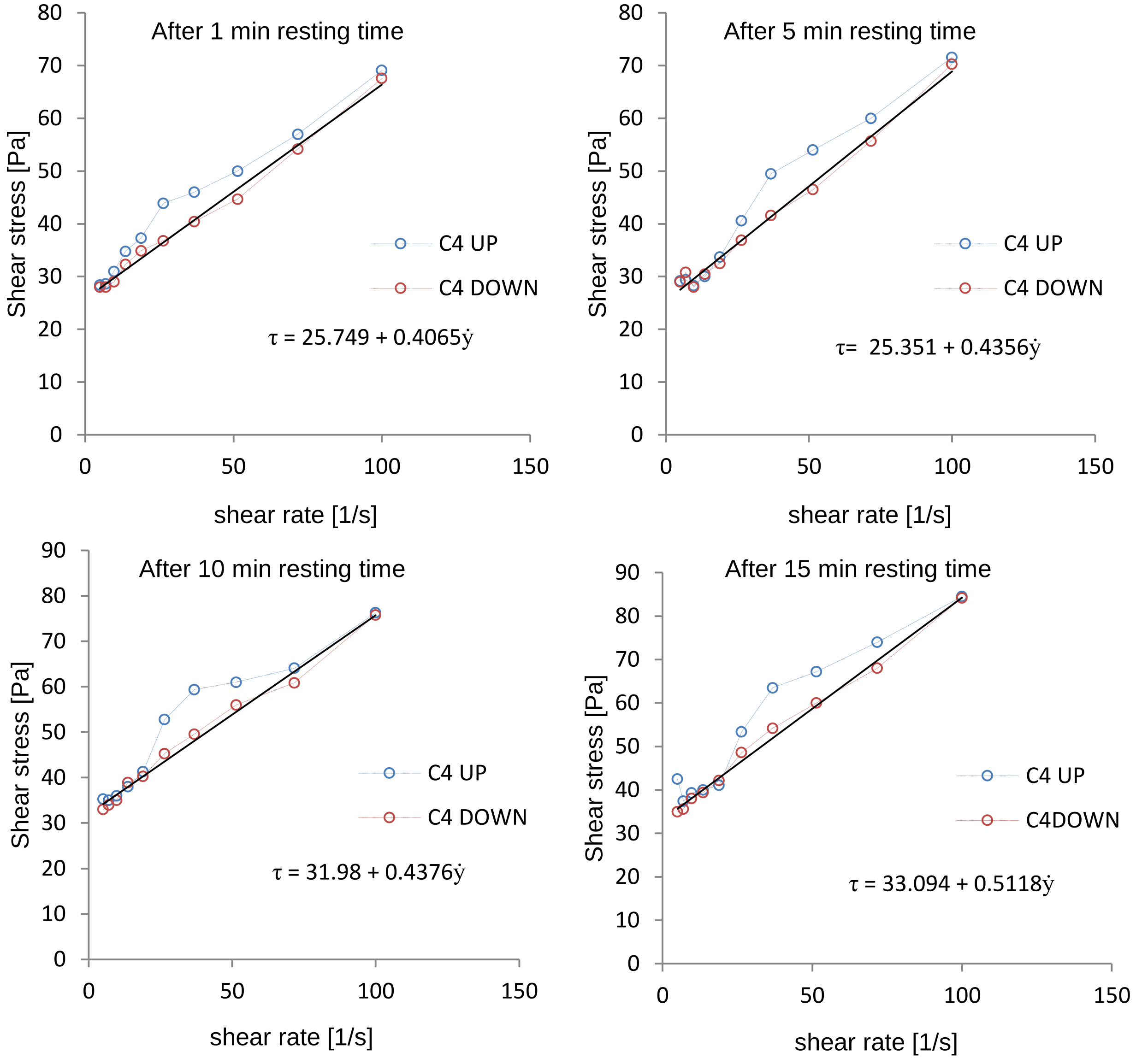


Figure C.3: Rheological parameters from hysteresis loop after different times for Cement C4 with no SP

Appendix D. Hysteresis loop of cements with SP1 (0.3%)

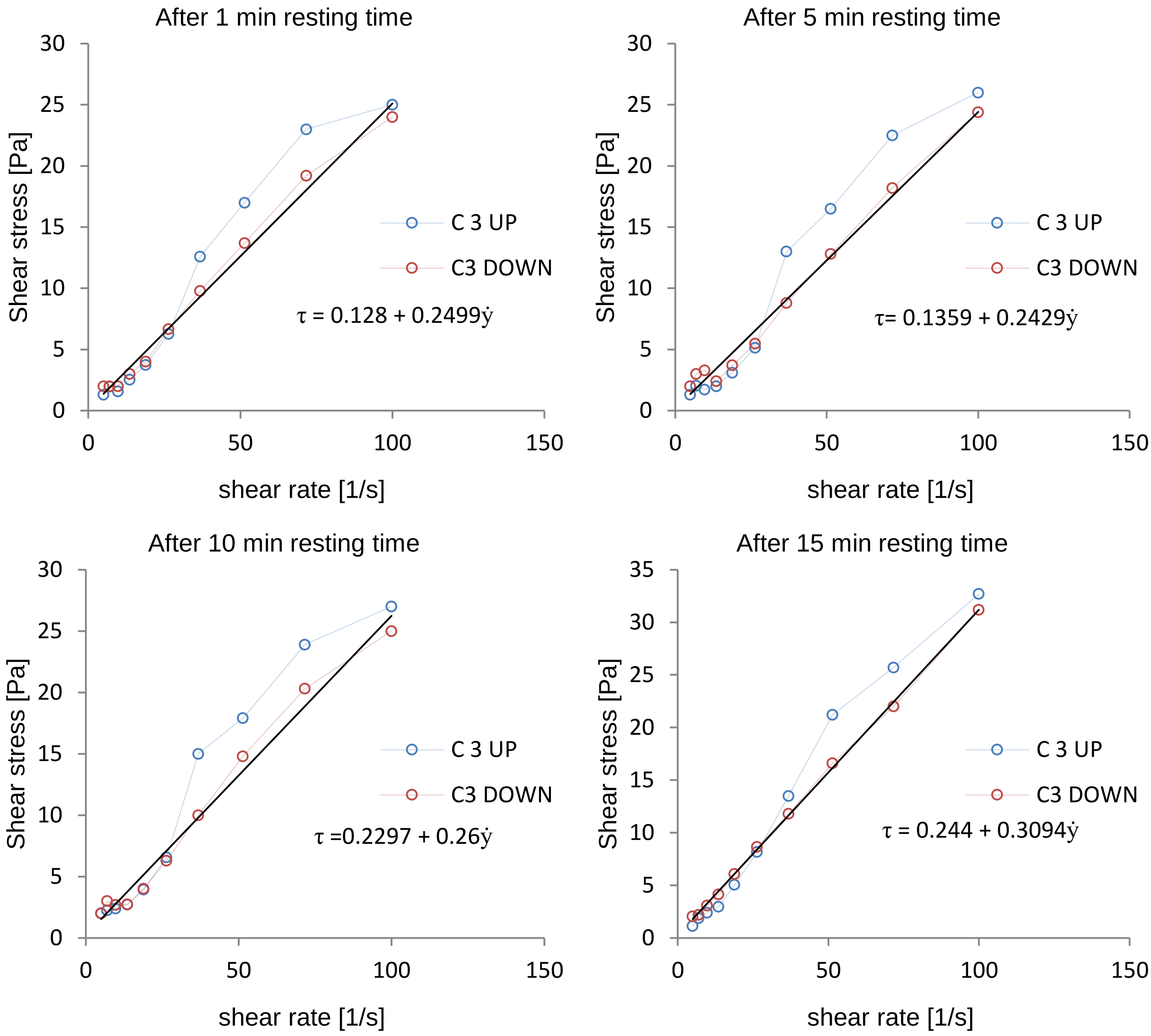


Figure D.1: Rheological parameters from hysteresis loop after different times for Cement C3 with SP1

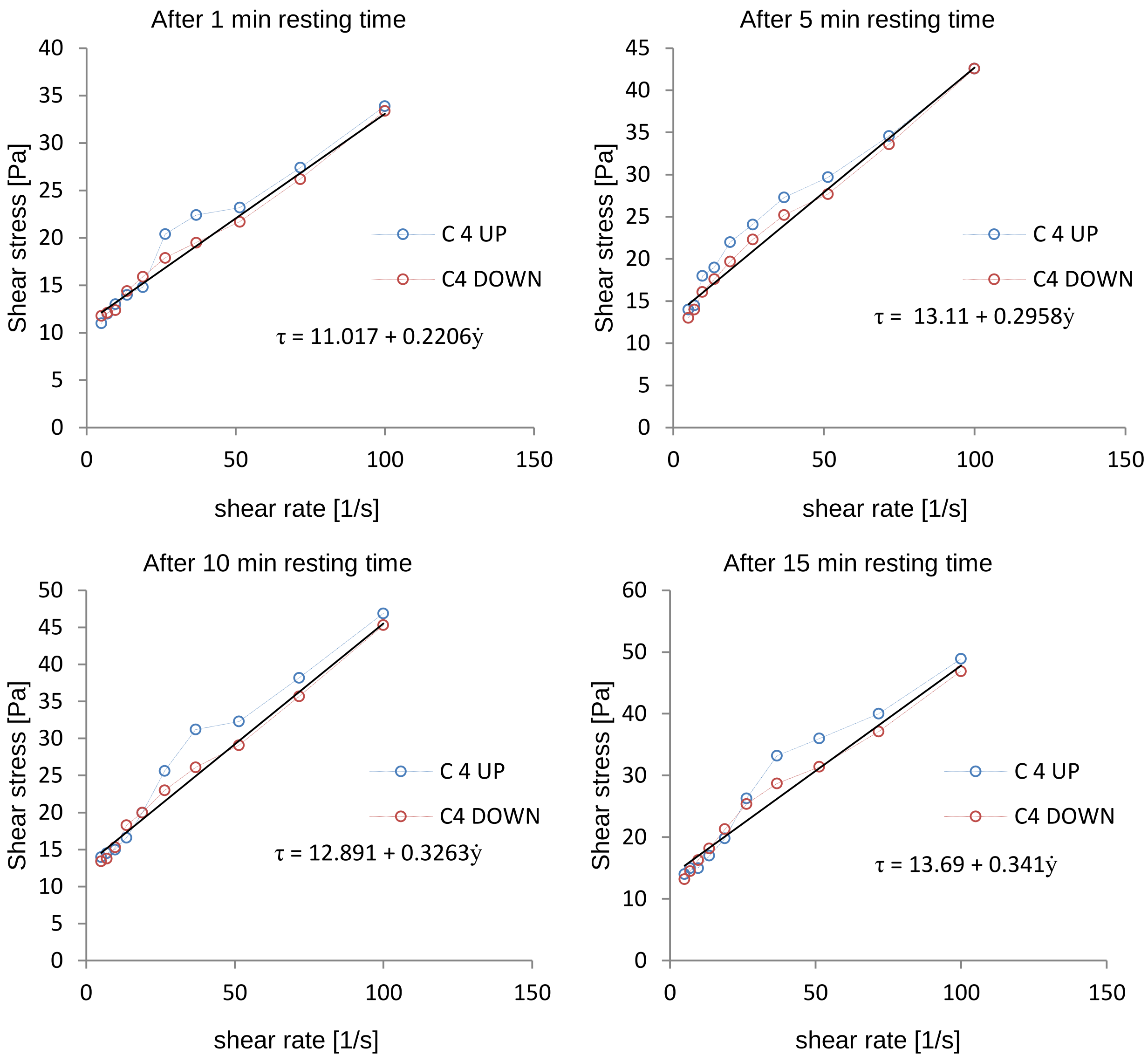


Figure D.2: Rheological parameters from hysteresis loop after different times for Cement C4 with SP1

Appendix E. Hysteresis loop of cements with SP2 (0.3%)

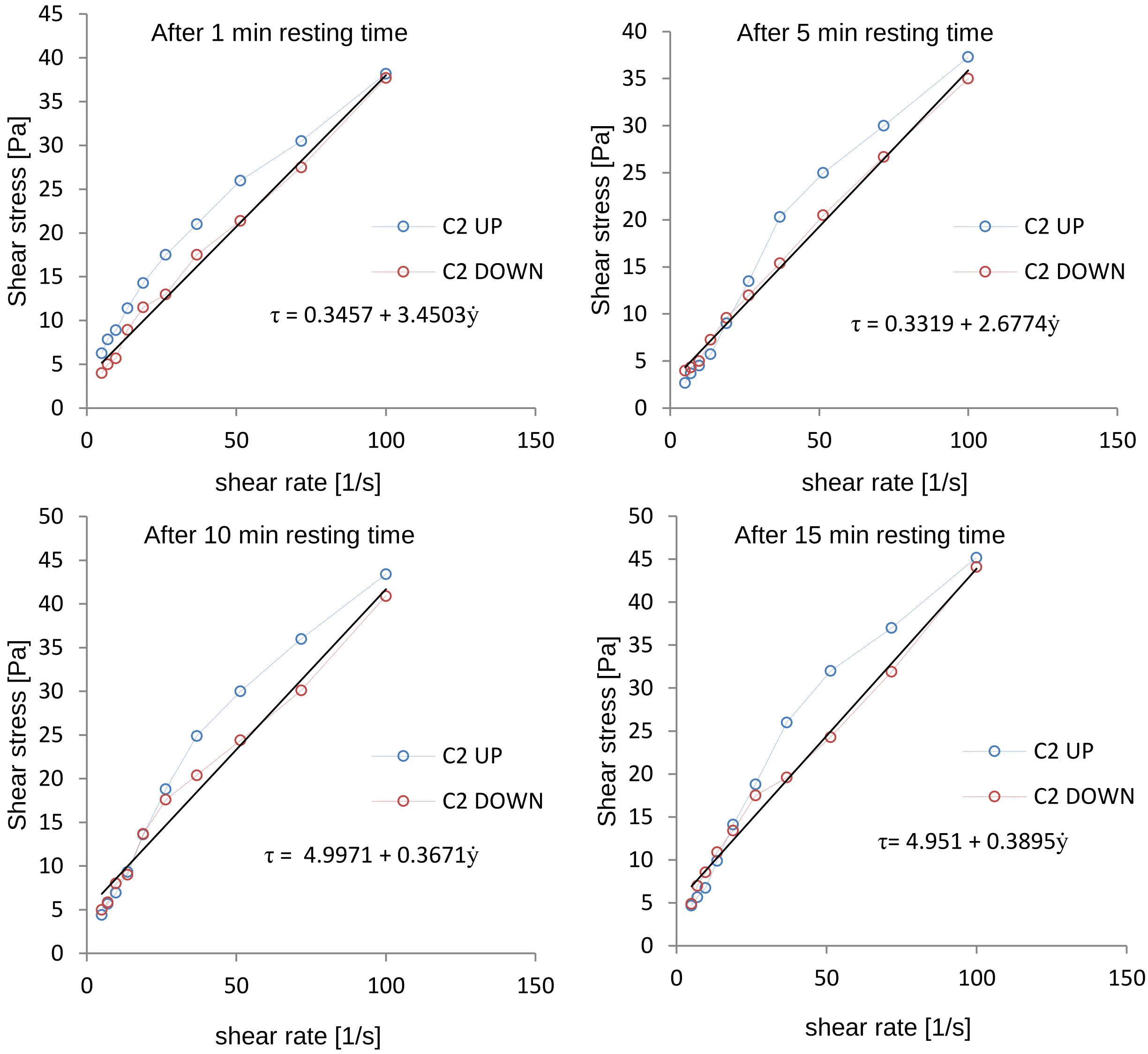


Figure E.1: Rheological parameters from hysteresis loop after different times for Cement C2 with SP2

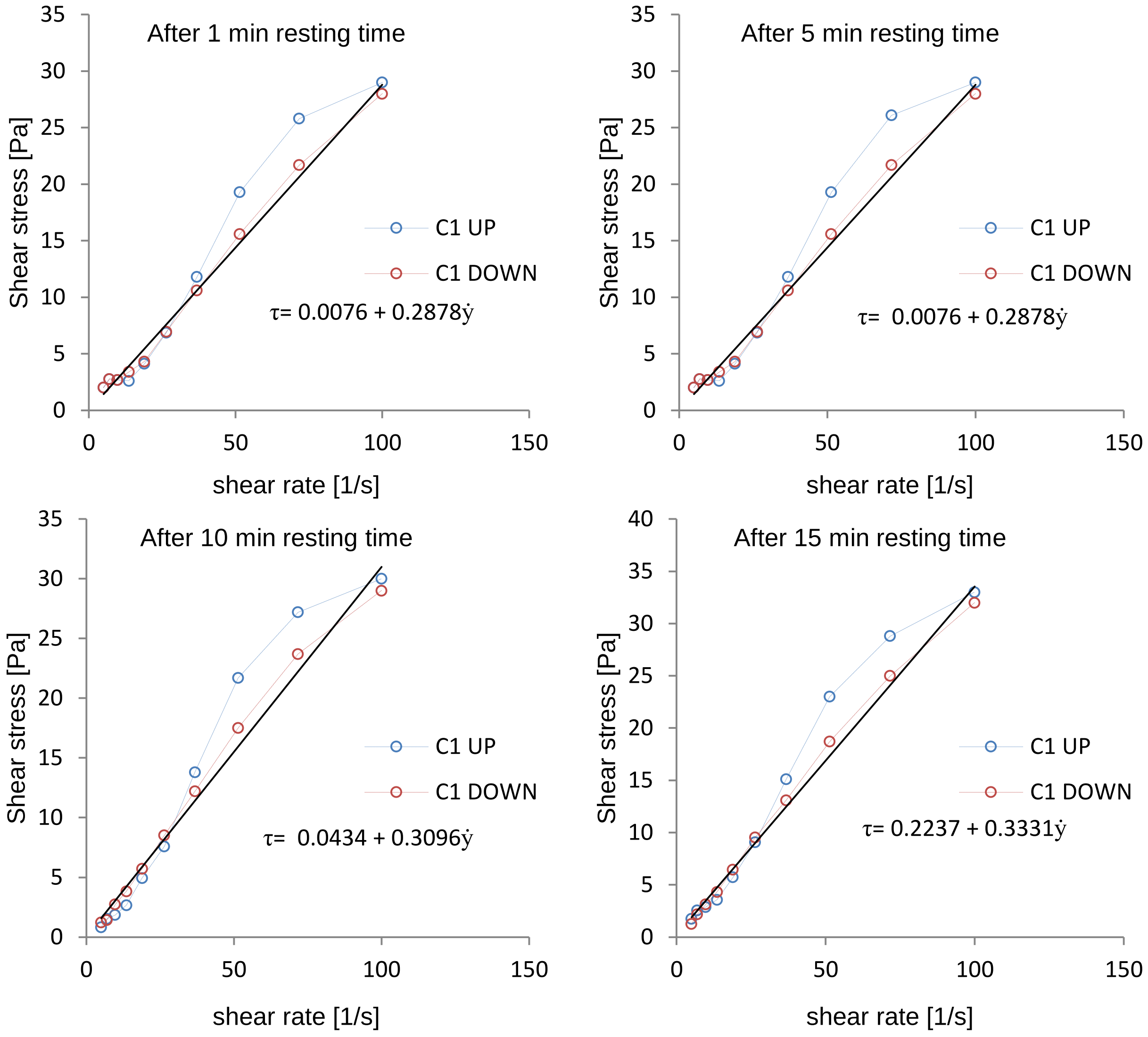


Figure E.2: Rheological parameters from hysteresis loop after different resting times of Cement C3 with SP2

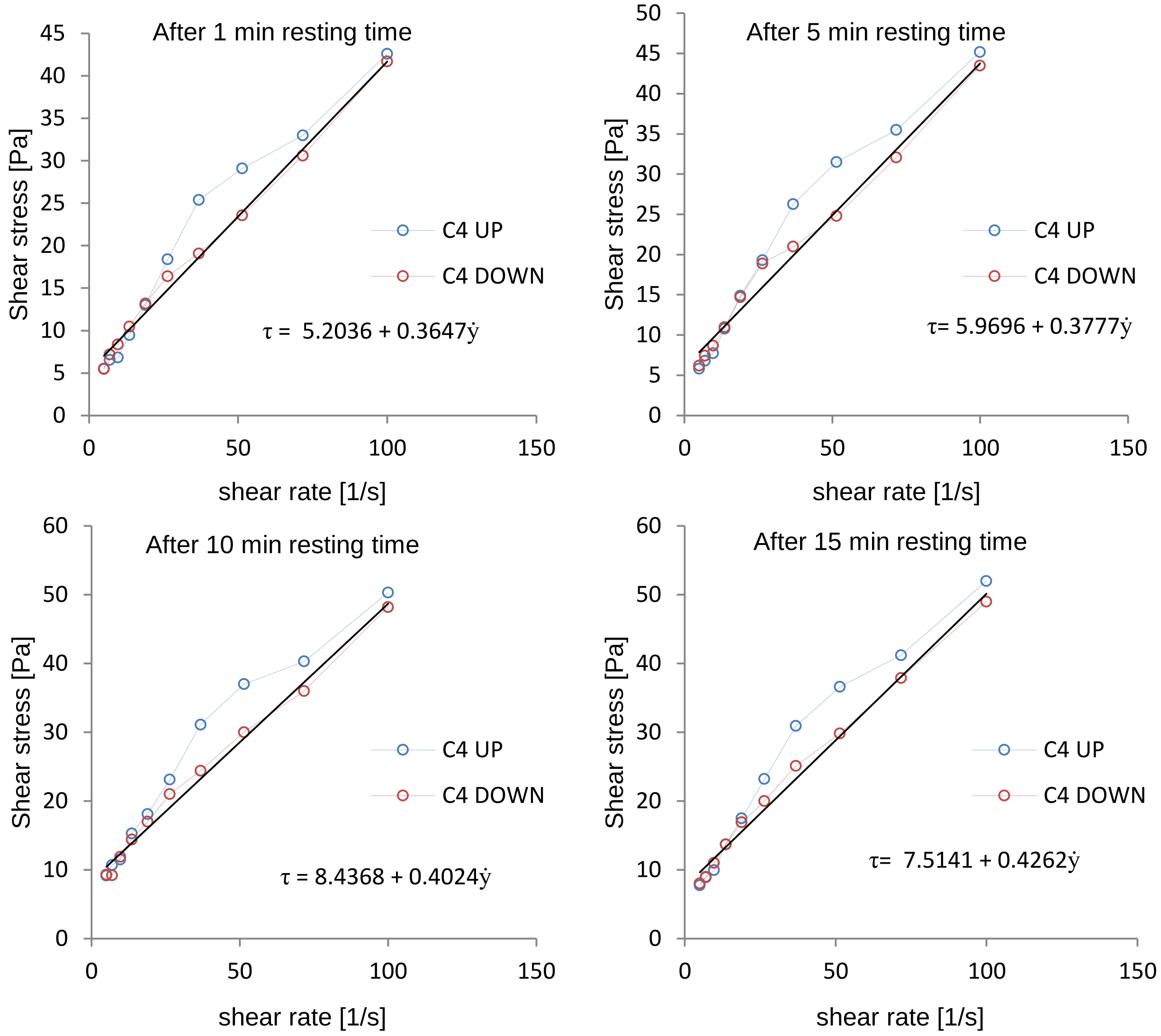


Figure E.3: Rheological parameters from hysteresis loop after different resting times of Cement C4 with SP2