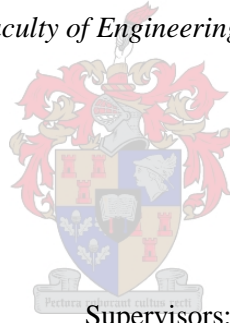# Developing a Low Embodied Carbon-content Concrete with Conventional Concrete Properties

By

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Thesis presented in fulfilment of the requirements for the degree of Master of Engineering (Research) in the Faculty of Engineering at Stellenbosch University

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Declaration

By submitting this thesis electronically, I declare that the entirety of the work contained therein is my own original work, that I am the authorship owner thereof (unless to the extent explicitly otherwise stated) and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Signature:

.…………………………………

Michael Andreas Diekmann

Date: April 2019

Abstract

In an ever-developing world, the use of concrete as a construction material, and cement as a main constituent thereof, is at a historical peak and set to increase even further in future. At the same time, the world is confronted with environmental challenges partly due to greenhouse gas emissions, to which the production of cement is a large contributor. In order to decrease the emissions and ensure greater sustainability of the concrete industry, it is therefore critical to reduce the cement content in conventional concrete. This reduction in cement content can however not sacrifice the quality of the concrete, in terms of certain properties that conventional concrete exhibits. It is therefore the main objective of this study to develop a low cement-content concrete, and as such a low embodied carbon-content concrete, with conventional concrete properties.

Three approaches of achieving this can be defined. Firstly, cement in concrete can be replaced by more environmentally friendly supplementary cementitious materials (SCM) or fillers. Furthermore, the water requirement of concrete can be reduced in order to achieve a lower cement content by, secondly, using superplasticisers or, thirdly, optimising particle packing. This study establishes reference mixes using the first approach, before separately using the latter two approaches to lower the water requirement of the former mixes at a constant slump and water/binder ratio. The three approaches are finally combined in order to establish what are termed the "optimised" mixes in terms of cement content, with conventional concrete properties being the aim.

The concrete properties that all mixes are evaluated for include rheological properties, setting time, compressive strength, permeability as part of durability and the equivalent carbon dioxide (CO_{2e}) emissions. Furthermore, certain indices showing the efficiency of use of cement and the CO_{2e} emissions due to the mixes in terms of compressive strength are determined. It was found that the replacement of various fractions of cement showed a pronounced reduction of CO_{2e} emissions, while resulting in mixes with conventional properties. The inclusion of superplasticisers improved the rheological properties of these mixes and further reduced the emissions of the mix, by significantly reducing the cement content. However, this decreased the compressive strength of the mixes. The optimisation of particle packing improved all the measured properties. The combination of all three approaches resulted in mixes with improved rheological properties, as well as a 40% to 60% decrease in the emissions due to the concrete. The compressive strength was negatively effected and halved compared to the reference mix. However, certain mixes still showed better efficiency indices than the reference mixes, meaning they used less cement and CO_{2e} emissions to develop strength. With regard to cement content, they could indeed be termed the "optimised" mixes.

Opsomming

Die gebruik van beton as 'n konstruksiemateriaal, en sement as 'n hoofbestanddeel daarvan, het historiese hoogtes bereik en verder groei word voorspel, weens die ekonomiese ontwikkeling van groot dele van die wêreld. Terselfdertyd word die wêreld met uitdagings in terme van ekologiese volhoubaarheid gekonfronteer, as gevolg van kweekhuisgasvrystellings. Hierdie vrystellings word tot 'n aansienlike deel veroorsaak deur die produksie van sement. Om meer volhoubaarheid van die betonbedryf te verseker is dit van uiterste belang om die sementinhoud van gewone beton tot 'n groot mate te verminder. Die eienskappe van die beton mag egter nie negatief beïnvloed word nie. Die doel van hierdie navorsing is dus om 'n beton met 'n lae sementinhoud, en sodanig 'n lae koolstofinhoud, met konvensionele beton eienskappe te ontwikkel.

Om die doel te bereik kan drie benaderings gevolg word. Eerstens kan gedeeltes van sement met omgewingsvriendeliker aanvullende sementagtige materiale (ASM) of vullers vervang word. Verder kan die waterbehoefte van beton verminder word om sodoende die sementinhoud te verlaag deur, tweedens, van superplastiseerders of, derdens, geoptimiseerde partikel verpakking gebruik te maak. In die navorsing word gewone betonmenge ontwerp deur die eerste benadering toe te pas, en dié menge word dan as verwysingsmenge gebruik. Daarna word die tweede en derde benaderinge afsonderlik gebruik om by konstante versakking en water/binder verhouding die waterbehoefte en, as gevolg hiervan, die sementinhoud van die menge te verlaag. Die drie benaderings word uiteindelik gekombineer om die "geoptimiseerde" menge in terme van sementinhoud te ontwikkel. Die menge word verder ook getoets om te bepaal of dit konvensionele betoneienskappe toon.

Die eienskappe waarvoor elke meng evalueer word sluit in: reologiese eienskappe, settyd, druksterkte, deurlaatbaarheid as deel van duursaamheid, en die ekwivalente koolstofdioksied (CO_{2e}) vrystellings. Sekere indekse wat die doeltreffendheid van die sementgebruik en CO_{2e} vrystellings in terme van druksterkte uitdruk word ook bepaal. Daar is bevind dat die vervanging van sement met ASM en vullers 'n aansienlike vermindering van CO_{2e} vrystellings veroorsaak, terwyl konvensionele eienskappe gehandhaaf word. Die gebruik van superplastiseerder het die reologiese eienskappe verbeter en CO_{2e} vrystellings verder verlaag, maar druksterkte is negatief beïnvloed. Die optimiseering van partikel verpakking het alle eienskappe verbeter. Die kombinasie van die benaderings het die reologiese eienskappe verbeter en die CO_{2e} vrystellings met 40% tot 60% verlaag. Druksterkte is egter negatief beïnvloed en gehalveer in vergelyking met die verwysingsmeng. Sekere menge het egter steeds beter doeltreffendheidsindekse getoon as die verwysingsmeng. Met betrekking tot die sementinhoud kan die menge inderdaad "geoptimiseerde" menge genoem word.

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Chapter 1

Introduction

In an increasingly developed and developing world, concrete has long been a widely used material. As a larger part of the world is set to industrialise, the importance of concrete is only set to rise. Due to the popularity of concrete, about 5500 Mt of cement are produced annually, and it is estimated that production will increase to 2.5 times this level by 2050, with most of this increase being attributed to the greater cement requirement in the developing countries (Müller & Harnisch, 2008; Scrivener, John & Gartner, 2016).

However, the use of concrete has significant environmental disadvantages, due to the high carbon dioxide (CO_2) emissions per ton of cement produced. Currently, these range from 800 to 900 kg CO_2 emitted per ton of cement produced, with a mass of 818 kg CO_2 per ton of cement taken as the average mass emitted during the production of ordinary Portland cement (OPC) in South African conditions (Cement and Concrete Institute, 2010). This makes OPC the constituent of concrete with the most unfavourable ecological footprint, and contributes to the fact that the cement industry produces 5% of annual CO_2 emissions due to human activity (Damineli, Kemeid, Aguiar & John, 2010). With the previously mentioned predicted increase in the use of concrete and, subsequently, cement, the emissions are set to increase sharply. With the growing environmental challenges and consciousness of these, it is thus of vital importance to make concrete a more environmentally sustainable material and to reduce its embodied carbon content, i.e. the CO_2 emitted during the production of concrete, due to materials and their processing. The measure set to make the most measurable difference in the CO_2 emissions per ton of concrete produced is thus obvious: the cement content per ton of concrete produced should be reduced.

The importance of providing solutions in this regard has been realised through a number of investigations, and it has been found that a reduction in the cement content of concrete can be achieved by two principal ways. Firstly, cement can be replaced by other, more sustainable materials, with as little adverse impact on the concretes properties as possible. Secondly, the water requirement of the concrete can be reduced, which, at a constant water/binder ratio, makes it possible to reduce the binder content, and as such the cement content. Furthermore, the latter can be achieved in two ways. Either a high range water reducing chemical admixture, i.e. a superplasticiser, can be included in the concrete, or the size fractions of the fine aggregate can be arranged in such a way that minimal voids exist between the particles, thus leaving little space in which water can be trapped. The latter

is referred to as optimised particle packing of the fine aggregate (Fennis, 2011; Proske, Hainer, Rezvani & Graubner, 2014).

Thus, the importance of reducing the cement content in conventional concrete has been highlighted, and techniques of achieving this pointed out. However, the success of the application of these techniques in reducing the cement content is highly dependent on the methodology used, as they are co-dependent in certain aspects. Furthermore, the materials used, and their physical and chemical properties have a large influence on the outcome. Due to this, an investigation needs to be carried out to determine the extent to which the cement content of conventional concrete, and accordingly its embodied carbon content, can be reduced.

1.1   Objectives and methodology

In order to achieve the greatest possible reduction in embodied carbon content of selected concrete mixes, this investigation aims to reduce the cement content of said mixes to the greatest extent possible. This is achieved by means of the following:

- Determining the greatest extent to which cement can be replaced by supplementary cementitious material (SCM) and filler at constant levels of workability, and while maintaining certain fresh and hardened properties that would be found in a conventional concrete without such cement replacement.
- Determining the greatest extent to which the water requirement and, subsequently, binder content at a constant water/binder ratio, of a conventional concrete mix can be reduced. This, by using varying water reducing chemical admixtures or optimising the particle packing of the fine aggregate of the mix, while maintaining constant levels of workability, and certain fresh and hardened properties that would be found in a conventional concrete without such reduction in binder content.
- Combining the replacement of cement by SCM and filler with the techniques of reducing the binder content in such a way that a concrete mix results that maintains constant levels of workability, and certain fresh and hardened properties also found in a conventional concrete with no such reduction of binder content.

1.2   Scope

The scope of this investigation into reducing the cement content of concrete while maintaining conventional properties is mostly restricted by the limits of practicality. As a further aim of this research is to provide practical results, i.e. results that could readily be implemented by industry, research has to be conducted in a way that maintains practicality. Firstly, this includes the selection

of materials, which should be readily and widely available and have economic benefits to a certain extent. Secondly, the process of preparing the aggregates for the concrete and mixing the concrete itself should not be complicated, in order to prevent the procurement of expensive equipment and any additional time intensive labour. In order for this element of practicality to be guaranteed, the scope of this research was limited so as to assure that the previously mentioned practical requirements could be met. Although this might have the effect of not presenting the concrete with the largest cement reduction possible, it nonetheless guarantees that the results of this investigation could be readily implemented in practice.

1.3   Outline of thesis

Chapter 2 provides a review of the literature available on the creation of low cement-content, sustainable concrete. Specifically, cement as a constituent of concrete is discussed and its shortcomings in terms of sustainability pointed out. Furthermore, the three approaches employed to reduce the cement-content of concrete in this investigation are studied in depth. Finally, reviews of similar work and manners in which the sustainability of concrete can be quantified are provided.

Chapter 3 lays out the experimental framework according to which this investigation was performed. This includes the broader methodology according to which cement-content was sequentially reduced for each of the three approaches, as well as the combination of these. Furthermore, information regarding the materials used, and the methodologies of the tests of the fresh, hardened and sustainability properties of the concrete is provided.

Chapter 4 provides the results of the investigation into replacing sizeable fractions of the cement content with supplementary cementitious materials and fillers, and discussions of these. In this regard, the mix designs of the newly established mixes are provided, as well as the results of the tests on the plastic and hardened properties of these mixes. Additionally, the sustainability properties of these mixes are discussed.

Chapter 5 shows the results and discussion of the inclusion of water reducing admixtures in the previously established mixes in Chapter 4, and the subsequent cement-content reduction due to this. The newly established mix designs are shown and discussed accordingly. Furthermore, the results of the tests on fresh, hardened and sustainability properties of these mixes are provided and discussed.

Chapter 6 provides the results and discussion of the optimised fine aggregate particle packing of the previously established mixes in Chapter 4, and the subsequent reduction in water requirement and cement-content. The newly devised mix designs are shown and discussed accordingly. Additionally, the results of tests on fresh, hardened and sustainability properties are provided and discussed.

Chapter 7 provides the results and discussion of the mixes established by combining the previously mentioned approaches of reducing the cement-content of concrete. With regard to this, the established mixed designs, as well as the results of tests on fresh, hardened and sustainability properties, are presented and discussed.

Chapter 8 provides the conclusions drawn from this investigation into reducing the cement-content of concrete. Furthermore, relevant recommendations for future work are provided.

Chapter 2

Literature Review

This chapter deals with the literature regarding the creation of a low embodied carbon concrete with conventional concrete properties. The global production of cement contributes 5% of annual global carbon dioxide (CO_2) emissions due to human activity, and a reduction of its use could therefore have vast potential environmental benefits (Damineli *et al.*, 2010). Environmentally friendly concrete has been designed differently in various research papers, using either varying binders or fillers to replace cement, or chemical admixtures and particle packing optimisation of the concretes aggregates to enable a reduction in the water requirement of the concrete (Fennis, 2011; Proske *et al.*, 2014). Thus, as part of this literature review, six focal sections are considered. Firstly, concrete and cement, as its main constituent, and their properties are defined. Subsequently, a section is devoted to the use of supplementary cementitious and waste materials to substitute a proportion of cement in concrete. In this regard, potential materials and their proportions in the concrete are discussed, as well as their influence on properties of the concrete and the embodied carbon content of the concrete. After this, the use of superplasticiser in concrete is discussed. Dosages and the environmental impact of superplasticiser is discussed. Following this, literature dealing with the particle packing density of aggregates of a concrete is discussed. As part of this, particle packing density is defined and various models to quantify packing density are discussed. Finally, ways in which the total carbon dioxide emissions during the lifetime of the concrete can be determined, as well as approaches of quantifying its sustainability, are discussed.

2.1 Concrete as a material and cement as its main constituent

Concrete can be defined as the solid mass created by the unification of cementing materials, i.e. cement (Damineli *et al.*, 2010). Due to the wide use of concrete as a material and the fact that cement is the constituent of concrete with the most negative contribution to concretes environmental footprint, it is important to understand and define the background and properties of concrete, and cement as concrete's main constituent.

2.1.1 Classifying cement

Generally, cement can be classified as a binder or glue, as known to the layman. In the presence of water, it forms a matrix binding aggregates in order to create a more rigid solid (Grieve, 2009).

The most widely used class of cement is the Portland Cement (PC) class. It can further be subdivided into subclasses, including Rapid Hardening Cement, White Portland Cement and Grey Portland

Cement (Alexandre, 2016). Ordinary Portland Cement (OPC) is the basis of this investigation and is focussed on in this section. OPC can further be classified as Type I, II, III, IV or V, respectively. These types of OPC have varying purposes: Type I is a general purpose cement while Type II offers extra durability in the form of additional sulfate resistance. Type IV OPC is a cement with a low heat of hydration and thus a slow reacting cement. Furthermore, Type III OPC provides high early strength and Type V OPC is resistant to sulfates, therefore being the most durable (Mehta & Monteiro, 2006; Thomas & Jennings, 2008).

2.1.2   Production process of cement

Initially, during the production of OPC, a blend between calcareous and argillaceous materials is finely ground. The calcareous material typically is limestone while argillaceous materials include clay and shale. This mixture is pre-heated to a temperature of 900°C in a process called calcination, in order for most carbon dioxide to be released. The carbon dioxide is not needed for the further processes and thus this is the phase in which most greenhouse gasses are released and waste products are generated. However, during this process the calcareous material is also reduced to slaked lime ($Ca(OH)_2$), an essential component of further phases of cement production (Ravina & Mehta, 1988; Kosmatka, Kerkhoff & Panarese, 2011).

Subsequently, during the transition phase, the mixture is fed into a rotary kiln running at a temperature of 1400 to 1500°C. During this phase, the physical properties of the materials change, with the material becoming slightly liquid. Additionally, the chemical properties of the materials change and the main components of clinker are formed, these being alite (C_3S), belite (C_2S), tetracalcium-aluminate (C_3A) and tetracalcium-aluminoferrite (C_4AF) (Ravina & Mehta, 1988; Kosmatka *et al.*, 2011). These components and the role they play in the reactions of cement are further explained in Section 2.2.1.

Thereafter, the clinker enters the sintering phase, during which further fuel for the reaction and air is introduced, while the kiln continues to run at temperatures of 1400 to 1500°C. This allows more belite to transform to alite (Kosmatka *et al.*, 2011).

Finally, the clinker reaches the cooling phase during which it is expelled from the kiln in the shape of chunks of solids. After cooling off, the clinker is finely ground and potential additives, such as fly ash and gypsum, are added, thus making the cement ready for use (Ravina & Mehta, 1988).

2.1.3   Properties of cement

2.1.3.1   *Physical properties*

When looking at the physical properties of cement, one needs to look at the individual particles of cement on a microscopic level. The individual particles are primarily of an angular nature, with particle sizes ranging from 2 to 80μm for most cements. However, this particle size is dependent on the grinding process and its extent, and particle sizes can be optimized according to the planned use of the cement (Domone & Illston, 2010). A scanning electron microscope (SEM) image of a typical cement particle can be seen in Figure 2.1, showing the typically angular particle shape.
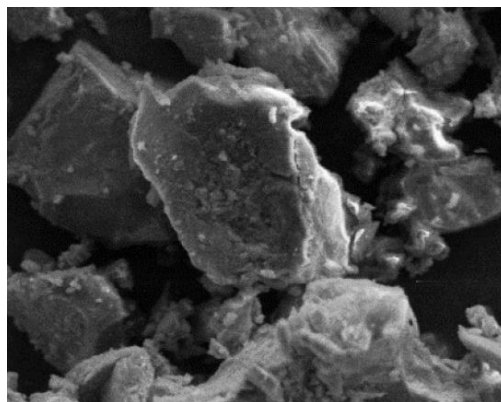
Figure 2.1: SEM image of a typical cement particle (Alexandre, 2016)

The need for particle size optimization becomes apparent when one considers the impact the fineness of the particles has on the reactivity of the cement, namely that finer cement has a higher reactivity. This is due to the higher surface area of finer cements, which in turn provides more opportunities for the hydration process to occur. The fineness of cement can be quantified using the Blaine test, measuring the resistance to air flow of a partially compacted cement sample, and thus the previously mentioned relationship between fineness and reactivity established (Domone & Illston, 2010; Alexandre, 2016).

2.1.3.2   *Chemical properties*

As mentioned in Section 2.1.2, the main chemical components of cement are alite (C_3S), belite (C_2S), tetracalcium-aluminate (C_3A) and tetracalcium-aluminoferrite (C_4AF). The abbreviations for these components are listed in Table 2.1, along with abbreviations of components of the chemical hydration reactions of cement which are explained in Section 2.2.1.1.

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Table 2.1: List of symbols denoting chemical components

Chemical component	Formula	Acronym
Calcium oxide	CaO	C
Silica	SiO_2	S
Water	H_2O	H
Aluminium oxide	Al_2O_3	A
Iron oxide	Fe_2O_3	F
Calcium hydroxide	$Ca(OH)_2$	CH
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A
Tetracalcium alumino-ferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

The frequency of calcium oxide and silica in the components of cement means that, generally, 60% to 67% and 17% to 25% of the weight of cement consist of calcium oxide and silica, respectively (Domone & Illston, 2010). These substances and the previously mentioned components they form with other substances aid the hydration reactions which are explained in Section 2.2.1.1. The fractions of these chemical components determine the properties of the cement. Table 2.2 summarises the impact they have on properties including the reactivity and durability of cement (Thomas & Jennings, 2008).

Table 2.2: Impact of chemical components on properties of various types of OPC (Thomas & Jennings, 2008)

Chemical characteristics	Cement properties
Above average C_3S content	Good early age strength development
Low C_3A content	Higher durability due to higher sulfate resistance
High C_3S content	High early age strength
Low C_3S and C_3A content	Slow reacting, low heat of hydration
Very low C_3A content	High durability due to high sulfate resistance

In addition to these components of cement, created during the burning of clinker in the kiln, additives are added to the cement once it has been expelled from the kiln. These could include gypsum, fly ash, slag and limestone. Their chemistry and impact on the properties of the cement are discussed in Sections 2.2.1, 2.2.3 and 2.2.4.

2.1.4 Properties of concrete and their definitions

2.1.4.1 *Workability and rheology*

Workability and rheology are properties that are applicable to concrete in its fresh, plastic state. Workability as such is a property that is difficult to define, and perhaps best put as "that property of

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freshly mixed concrete or mortar which determines the ease with which it can be mixed, placed, consolidated and finished to a homogeneous condition" (American Concrete Institute, 2000). Furthermore, workability is a property that can only be measured directly to a certain extent, by a number of established methods. However, experienced concrete technologists are likely to give an informed objective assessment of concrete in terms of two factors, namely concrete's consistence and cohesiveness. Consistence describes the ease with which concrete flows and relates to how wet or dry a particular concrete mix is. Wet concrete mixes are typically more workable than dry ones, but concrete mixes with equivalent consistencies could have varying workabilities. Consistence is typically measured by the slump test, amongst others. Cohesiveness describes the ability of a mix to resist segregation and bleeding, i.e. a very cohesive mix is not prone to segregation and bleeding. An objective judgement is needed to establish the degree of cohesiveness of a concrete mix, as no explicit test methods exist (Kellerman & Crosswell, 2009).

A more exact way of quantifying the concept of workability is the science of rheology. This science deals with the flow and deformation of fluids, solids and gasses, but is, however, mostly applicable to fluids. Due to the fact that fresh concrete can be considered a fluid, its rheology can be studied. However, the fact that the rheological properties of concrete are time dependent and can vary widely due to a wide range of materials used, complicates the subject. Nonetheless, concrete can be simplified as "a concentrated suspension of aggregate in cement paste", and thus use can be made of the vast amount of research that exists on the rheology of concentrated suspensions (Koehler & Fowler, 2004).

Contrary to an elastic solid, a viscous liquid continuously deforms when a shear stress is applied to it, and this deformation is not recovered once the stress is no longer applied. In terms of the shear stress in an elastic solid, the relationship can be described by:

$$\tau = G\gamma$$

(2.1)

which shows that the shear stress τ in an elastic solid is directly proportional to the shear strain γ, with the shear modulus G relating the two. Similarly, for viscous liquids like concrete, the shear stress and the rate of the application of shear strain are related by:

$$\tau = \eta\dot{\gamma}$$

(2.2)

with τ being the shear stress, η representing the coefficient of viscosity and $\dot{\gamma}$ representing the shear rate. This equation thus states that the higher the rate at which a viscous fluid is sheared, the greater the required shear stress is. It thus represents one specific combination of shear stress and shear rate for steady flow of a liquid material. However, in order to determine the rheology of a liquid, the

properties over a wide range of shear stresses and shear rates need to be known. To make this possible, various models of flow curves have been devised, relating shear stresses and shear rates. The two most basic and most used relationships are elaborated on here, namely the Newtonian and Bingham model (Koehler & Fowler, 2004).

The Newtonian model follows Equation 2.2, thus assuming that there is a linear relationship between shear stress and shear rate. Furthermore, it assumes that the flow curve of a liquid intercepts the shear stress axis at the origin, as shown in Figure 2.2. These assumptions are basic and thus do not adequately reflect the behavior of most fluids, due to the non-linear behavior of these, with concrete being one such fluid. More specifically, concrete and similar fluids possess a minimum yield stress which must be exceeded before flow of the fluid can take place. This is illustrated in a basic manner by the slump test usually performed on concrete in its fresh state. Namely, as the slump cone is lifted, gravity induces a stress in the concrete which causes it to flow briefly. When the gravity induced stress becomes smaller than the minimum yield stress of the concrete, the concrete stops flowing. This behavior is illustrated by the Bingham model, which includes a term for the minimum yield stress of a material, often referred to as static yield stress, and is governed by:

$$\tau = \tau_0 + \mu\dot{\gamma}$$

(2.3)

with the model being illustrated in Figure 2.2. As can be seen from the equation, similarly to the Newtonian model, the Bingham model assumes linear behavior, while incorporating a term for the minimum yield stress, τ_0. The variable μ represents plastic viscosity, which refers to the same physical relationship as the previously mentioned viscosity, η. Thus, only the yield stress and plastic viscosity need to be determined. This, combined with the accuracy of the Bingham model in predicting even the behavior of material with non-linear flow behavior for low shear rates, make it the most widely used model (Koehler & Fowler, 2004).

Viscosity can be defined as the coefficient relating the shear stress and shear rate of a fluid, thus being a constant for a Newtonian fluid, as can be deduced from Equation 2.2. However, for non-Newtonian behavior, viscosity is defined differently. For instance, to define the plastic viscosity used with regard to the Bingham model, firstly, differential viscosity, η_{diff}, needs to be defined as the derivative of shear stress with regard to shear rate, given by:

$$\eta_{diff} = \frac{\partial \tau}{\partial \dot{\gamma}}$$

(2.4)

In turn, the plastic viscosity, μ, is defined as the limit of the differential viscosity as the shear rate approaches infinity, as shown by:

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$$\eta_{pl} = \mu = \lim_{\gamma \to \propto} \frac{\partial \tau}{\partial \dot{\gamma}}$$
(2.5)

When the Bingham model is used, it is assumed that the plastic and differential viscosity are equal for all shear rates (Koehler & Fowler, 2004).

The yield stress of a material is a complex term to define and has led to much debate. It has previously been defined as the stress related to the force required to break down a materials structure and initiate the flow thereof. For the previously mentioned Bingham model, it is obtained by tracing back the graph provided by the shear rate and corresponding shear stress coordinates, to the shear stress axis, this intercept providing the yield stress. This can be seen in Figure 2.2. It is thus assumed that if the possibility to measure shear stress at very low shear rates existed, this yield stress could be accurately measured. This theory has been debated extensively, with some research concluding that flow will occur at all shear rates, however low they are, and that no static yield stress exists as such (Barnes & Walters, 1985). It was similarly found that concrete mixtures subjected to vibration behave as Newtonian fluids at low shear rates, again disagreeing with the concept of yield stress (Tattersall, 2014). Nonetheless, for conventional research yield stress is a term with practical significance, as it describes the rheology of concrete to a sufficient extent. However, a careful distinction has to be made with regard to the method of measurement. Firstly, static measurements, taking place when the material is at rest initially, often result in higher values of yield stress, often referred to as the static yield stress. On the contrary, dynamic measurements of the flow curve, taking place when the material has already been disturbed, result in lower values, often referred to as the dynamic yield stress. While this difference has to be carefully interpreted, both values give a means of quantifiably comparing two concrete mixes in terms of their practicality. Particularly, a lower yield stress indicates a greater ease of placing (Koehler & Fowler, 2004).
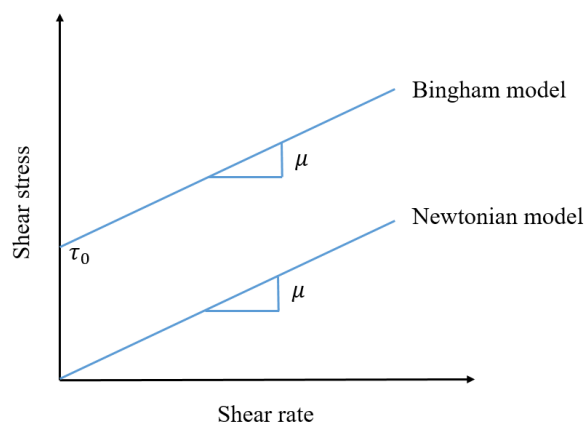
Figure 2.2: Graph of Bingham and Newtonian rheological models (Koehler & Fowler, 2004)

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2.1.4.2   *Setting time*

The term "setting time", when used with regard to concrete, refers to the period of time taken for a change in the physical and chemical properties of the cementitious paste of concrete to occur, namely that from the plastic to rigid state. It is measured by taking note of the penetration resistance of the cementitious paste over the previously mentioned period of time. The changes of the physical and chemical properties of the concrete do not occur at an uniform rate, rather following exponential trend when considered over time, as seen in Figure 2.3 (Mehta & Monteiro, 2006). Furthermore, two major phases are identified within the setting time: the time until initial set and until final set of the concrete. Initial setting time is defined as the time after which the concrete can no longer be handled without causing substantial damage to its internal structure. Final setting time is defined as the time after which concrete is considered a rigid material, as it has lost all of its plasticity. Additionally, the time between mixing and final setting time is divided into various phases, describing the changes occurring in the respective phases. In the dormant stage, which occurs before initial set, the paste is in a plastic, workable state. During the setting stage, which occurs between initial and final set, the paste is stiff and no longer workable. The phase after final set is known as the hardening stage, during which the concrete is rigid and gains strength over time (Grieve, 2009).
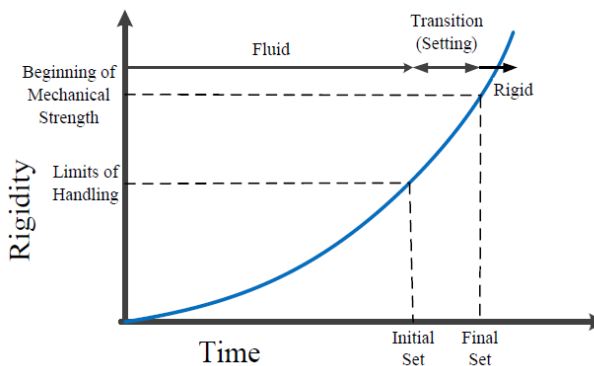
Figure 2.3 Development of concrete rigidity with regard to time (Mehta & Monteiro, 2006)

2.1.4.3   *Compressive strength*

The compressive strength of concrete is perhaps the property that gives concrete the greatest practical value. It can be defined as the maximum uniaxial load, applied at a particular rate that can be sustained by a concrete specimen, in relation to the cross-sectional area of that specimen. This cross-sectional area has to be constant with plane, parallel ends which are at right angles to the axis of the specimen.

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The load has to be applied between rigid, flat plates. In this regard, failure is defined as the maximum stress that can be withstood before excessive deformations occur, even when no other external signs of failure are present (Perrie, 2009).

The compressive strength of conventional concrete is mostly dependent on the water/binder ratio, followed by the total cement content, cement type, fineness of cement, age of the concrete, the curing temperature and if sufficient moisture is available for it to develop strength. As the water/binder ratio increases, the strength decreases. Furthermore, higher cement contents result in a stronger hydration reaction and higher compressive strength. The fineness of the cement influences the compressive strength in such way that a finer cement usually results in higher strength, due to increased surface area and reactivity (Zhang & Napier-Munn, 1995; Grieve, 2009). Finally, the compressive strength is usually measured at certain ages, and, when tested under typical laboratory conditions, concrete is cured in water tanks at prescribed temperatures. Furthermore, specimen sizes are also prescribed for laboratory conditions, with cube moulds being used, as required by specific standards (SANS, 2006a; Perrie, 2009).

The compressive strength of concrete can also be dependent on the addition of supplementary cementitious materials as discussed in Section 2.2.3.6.

2.1.4.4   *Durability*

Durability, with regard to concrete, can be defined as concrete's ability to withstand the adverse impacts of its environment without loss of serviceability or the need for repair, over the course of its service life. The adverse impacts it could experience over its service life can be of varying nature, both physically and chemically affecting concrete. The transport mechanism of these negative impacts can be of importance when predicting the durability of concrete, and three primary mechanisms can be identified (Ballim, Alexander & Beushausen, 2009).

Firstly, the movement of liquids through the structure of the concrete under an external pressure is identified as one such mechanism. This mechanism is known as permeation. Therefore, the term permeability refers to the extent to which fluids can move through concrete, and is mainly dependent on the structure of concrete, as well as the degree of moisture in the concrete and the properties of the fluid moving though the material. The microstructure of concrete is mostly dependent on the type and amount of binder and aggregate, as well as water/binder ratio and overall mix design, all of which determine the volume of voids for fluids to permeate through. A higher permeability could have negative impacts on the durability, as fluids could attack reinforcing steel in the concrete and

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carbonation of the concrete could increase. The permeability of concrete can be evaluated by tests such as the oxygen permeability index test (OPI) (Ballim *et al.*, 2009).

Secondly, absorption is identified as a transport mechanism having an adverse effect on concrete. This mechanism involves a fluid being drawn into unsaturated, porous concrete in the presence of a capillary force. This force is dependent on the extent to which the concrete is saturated and the structure of the pores of the concrete. The rate at which this process occurs is defined as the sorptivity of the concrete. The overall sorptivity of the concrete is dependent on the degree of interconnection between larger pores, and thus by the orientation and distribution of the aggregate, as well as the mix composition and compaction of the concrete. The sorptivity can be evaluated by tests such as the water sorptivity test (Ballim *et al.*, 2009).

Finally, the third major transport mechanism is diffusion. Diffusion is the movement of liquids, gasses or ions through a porous concrete due to a concentration gradient. Partially or fully saturated concrete which is exposed to salts is particularly vulnerable to this transport mechanism. By absorption, high salt concentrations are developed at the surface of the concrete. Due to the lower concentrations of salt inside the concrete, diffusion causes the salt to migrate. The rate of this process is dependent on the moisture content of the concrete, temperature and presence of cracks and voids. The chloride conductivity test can be used to establish the extent of this transport mechanism (Ballim *et al.*, 2009).

2.2   Supplementary cementitious materials and fillers

The use of supplementary cementitious materials and non-reactive fillers can aid the designer in lowering the cement content while still maintaining workability requirements. However, it is important to note the impacts, both positive and negative, that these materials can have on the concrete mixture, in both the fresh and hardened state.

2.2.1   Supplementary cementitious materials

Supplementary cementitious materials (SCM) can be described as binders, similar in nature to the primary binder, namely ordinary Portland cement (OPC). A binder, and as such a SCM, can be defined as a material that through a chemical process and reaction, creates a bond between the inert particles of the concrete mixture. Three types of reactions forming cement gel commonly occur and as such three types of binder particles exist: hydraulic particles, latent hydraulic particles and pozzolanic particles. The cement gels formed differ for each reaction and different material used, and as such yield concrete mixes with different properties.

2.2.1.1 *Hydraulic particles*

OPC can be described as consisting of hydraulic particles, due to the fact that it reacts with water to form a cement gel, giving concrete its strength. The reaction can be described by:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{2.6}$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \tag{2.7}$$

$$C_3A + CH + 12H \rightarrow C_4AH_{13} \tag{2.8}$$

$$C_4AF + 4CH + 22H \rightarrow C_4AH_3 + C_4FH_{13} \tag{2.9}$$
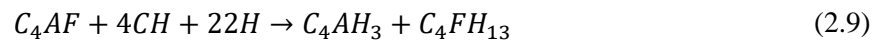
with the abbreviations being listed in Table 2.1 (Grieve, 2009).

The reactions described in Equations 2.6 and 2.7 occur rapidly in comparison to the other two types of reactions. During the reaction the calcium silicate hydrate gel ($C_3S_2H_3$), previously described as cement gel, and calcium hydroxide ($Ca(OH)_2$), otherwise known as lime, are formed (Fennis, 2011). Tricalcium silicate and dicalcium silicate are the main reactants for the calcium silicate hydrate gel, with tricalcium silicate reacting quicker than dicalcium silicate, and being responsible for the early-age strength gain while the latter is responsible for long-term strength (Zhang, Gao, Gao, Wei & Yu, 2013). Tricalcium aluminate and tetracalcium alumino-ferrite contribute less towards strength gain of the concrete. Furthermore, tricalcium aluminate can cause flash set of the cement paste when reacting with water. To counter this, gypsum ($CaSO_4 \cdot 2H_2O$) is added to the cement. This reacts with tricalcium aluminate and slows down the reaction causing flash set (Grieve, 2009).

2.2.1.2 *Latent hydraulic particles*

Similarly to hydraulic particles, latent hydraulic particles also react with water to form a silica-alumina gel which surrounds the particles (Czernin, 1980; Kurdowski, 2014). However, the reaction of latent hydraulic particles with water takes place slower than that of the hydraulic particles with water and needs to be activated by alkalis or sulfates. The slow reaction is due to the silica -alumina gel prohibiting the contact of the latent hydraulic particles with water. However, when a strong alkaline substance is present, the silica-alumina gel has a coarser texture and higher permeability. This is favourable for the rate of reaction, as more contact takes place between the latent hydraulic particles and water. As previously mentioned, the reaction between hydraulic particles and water yields calcium hydroxide, an alkaline substance. This reaction is thus well suited to activate and

accelerate the reaction between water and latent hydraulic particles. Although the theory behind these reactions is understood to a certain extent, the reactions are complex and have been simplified by:

$$3(C + S) + 3H \rightarrow C_3S_2H_3 + S \tag{2.10}$$

$$a(S) + b(CH) + Other \rightarrow C_3S_2H_3 + CA \tag{2.11}$$
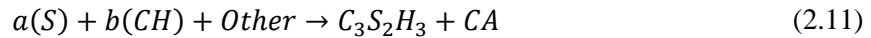
An example of a type of latent hydraulic particle is ground granulated blast surface slag (GGBS). It is represented by *(C+S)* in this case, while *a* and *b* are the constants required for stoichiometric equilibrium. "*Other*" refers to yet unknown substances required for equilibrium (Fennis, 2011).

2.2.1.3   *Pozzolanic particles*

On the contrary, pozzolanic particles do not react with water but with the calcium hydroxide produced by the reaction between OPC and water, in order to yield a cement gel. This reaction is given by:

$$2S + 3CH \rightarrow C_3S_2H_3 \tag{2.12}$$

The extent of the pozzolanic reaction depends on the amount of calcium hydroxide present in the mixture. It is thus common that this reaction is only triggered when the reaction between OPC and water is at an advanced stage and more calcium hydroxide has been produced, thus resulting in later strength gain of concrete when pozzolanic material is included. However, characteristics of the individual particles also influence the speed of the reaction: finer particles tend to react faster than coarser. An example of a pozzolanic material is fly ash and silica fumes (Fennis, 2011).

2.2.2   Fillers

Fillers are defined as materials which are chemically inert and as such have no binding ability, and thus produce no cement gel and add little strength to concrete. Although they do not add strength to the same extent that binders do, they nonetheless possibly have a positive effect on various other properties of concrete. By filling voids in the concrete, fine fillers improve the packing density of the concrete and reduce the water demand of the concrete (Fennis, 2011). Furthermore, these fillers disperse cement grains by altering the orientation and formation of cement particles. This further improves the packing density of the concrete mix (Bonavetti, Donza, Menendez, Cabrera & Irassar, 2003).

Furthermore, fillers can act as nuclei to which cement gel can attach and can act as a crystallization nucleus for the reaction of calcium hydroxide ($Ca(OH)_2$) (Bonavetti *et al.*, 2003). This accelerates the hydration of clinker minerals, one of these being tricalcium silicate, thus resulting in faster

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strength gain. Fine fillers are deemed to be particularly effective in this regard as they provide more surface area for nucleation and cement gel to attach to. Fillers with a Blaine specific surface area greater than 16 000 cm^2/g have been found to have a noticeable effect in this regard. Ground limestone ($CaCO_3$) is an example of a chemically inert filler that can be included in concrete (Bosiljkov, 2003; Proske *et al.*, 2014).

2.2.3   Fly ash

2.2.3.1   *Origin of fly ash*

Fly ash is a byproduct that is formed during the burning of coal, for instance during the process of power generation in coal fired power stations. Although these type of power stations are slowly being phased out in favour of more environmentally friendly forms of power generation, they are still used extensively internationally, and especially in South Africa (Jeffrey, 2005). Fly ash thus remains a material that is widely available and would otherwise be discarded if not used in concrete (Rivera, Martínez, Castro & López, 2015).

2.2.3.2   *Chemical composition*

While the chemical composition of fly ash is mostly dependent on the type of coal burnt and its quality, its main constituents are silica, alumina, and calcium and iron oxides, respectively. These originate from inorganic material contained in the coal which disintegrates during the burning process (Xu, 1996; Joshi & Lohita, 1997). Two main types of fly ash can be defined, which are specified to be Class C and Class F fly ash. Class C fly ash is obtained from the burning of sub-bituminous or lignite coal, while Class F fly ash is obtained from the burning of bituminous or anthracite coal. The types of coal burnt further influence the calcium content of the types of fly ash, with sub-bituminous or lignite coal producing high calcium content fly ash, and bituminous or anthracite coal producing low calcium content fly ash. The varying calcium contents have an impact on the amount of oxides formed during the burning of the coal, namely silica, alumina and iron oxides. The amounts of these are used to classify fly ash, with fly ash in which these oxides exceed 70% by weight being classified as Class F, and fly ash in which these oxides exceed 50% by weight being classified as Class C (Xu, 1996).

Furthermore, the lime content of fly ash can be used to distinguish it. If fly ash contains more than 10% free lime by weight it is considered to have a high lime content. This affects the content of iron oxide, as this is lower for fly ash with high lime content. The greater amounts of calcium that follow from this affect the self cementing capacity, as is obvious when the previously mentioned reactions of cement are considered, shown in Equations 2.6 to 2.9 (Xu, 1996). Table 2.3 summarises the chemical composition of varying classes of fly ash (Alexandre, 2016).

Table 2.3: Chemical composition of varying fly ash types

Fly ash type	CaO (%)	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	MgO (%)
Class C (Domone & Illston, 2010)	8-40	27-52	9-25	4-9	2-8
Class F (Domone & Illston, 2010)	1.5-6	44-58	20-38	4-18	0.5-2
South African (Grieve, 2009)	4-7	48-55	28-34	2-4	1-2

2.2.3.3   *Physical properties*

When looking at the physical properties of fly ash particles, the particle shape, sizes and surface texture are found to be of primary importance, as these contribute to the final concrete properties. Fly ash particles are primarily spherical in shape, and the impact of this is discussed in subsequent sections. The particle sizes of fly ash are smaller when compared to those of ordinary portland cement and generally range from 1 to 80 μm. However, this is dependent on the production process of fly ash and can vary (Grieve, 2009; Domone & Illston, 2010). Finally, fly ash particles typically have a smooth surface texture, the impact of this again being discussed in following sections (Koehler & Fowler, 2004). A scanning electron microscope (SEM) image, showing the spherical particle shape and smooth texture of a typical fly ash particle can be seen in Figure 2.4.
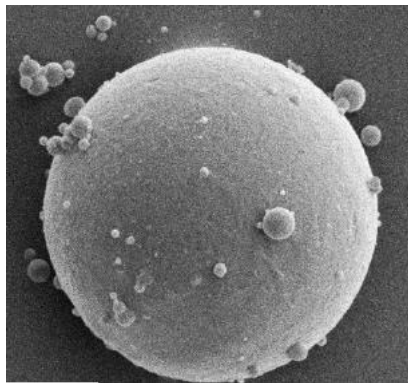
Figure 2.4: SEM image of a typical fly ash particle (Alexandre, 2016)

2.2.3.4   *Influence on workability and rheology*

Generally, fly ash is known to have a positive effect on the workability of concrete, as it decreases the amount of water required for concrete to reach certain slumps. Conflicting mechanisms contribute to the influence of fly ash on workability. Firstly, fly ash particles are smaller than cement particles, which results in a larger surface area which needs to be wetted, thus reducing the workability. Conversely, fly ash particles are spherical in shape and of smooth texture. This allows coarse particles to flow past easily and has a positive influence on workability (Koehler & Fowler, 2004).

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The influence of fly ash on the rheology of concrete is twofold. Fly ash is known to reduce the yield stress of concrete, while having varying effects on the viscosity. It has been shown that when fly ash has been used on a mass replacement basis in concrete, it reduced the yield stress significantly and plastic viscosity slightly (Tattersall, 2014). This reduction was greatest when initial cement contents were lower. However, the reductions in yield stress and plastic viscosity were doubled when fly ash was replaced on a volume basis, showing that the greater surface area had a bigger impact on the difference in volume of the mass and volume replacements. A replacement level of 10% by fly ash has been shown to actually increase the yield stress of concrete (Szecsy, 1997). However, replacement levels of 10 to 20% have shown the previously mentioned reduction in yield stress. Replacement levels of 5% have shown a marked reduction of plastic viscosity of concrete, but little additional reduction has been noted with higher replacement levels.

2.2.3.5   *Influence on setting time*

As mentioned in Section 2.2.1, the setting time of concrete is mostly dependent on the amount of tricalcium-aluminate (C_3A) and tricalcium-silicate (C_3S) present in the reaction of OPC with water, with tricalcium-aluminate being responsible for possible "flash-set" and tricalcium-silicate for the early-age strength gain (Grieve, 2009).

Fly ash is widely known to delay the setting time of concrete, as it has a retarding effect. There are numerous reasons for this effect, the first of these being the dilution effect. This effect describes the partial replacement of cement with a SCM, and the following decrease in initial reactants, particularly calcium, available. This delays the reaction, as it is very much dependent on calcium, as previously mentioned. Fly ash has been shown to be both low in calcium and a "calcium sink", by removing calcium ions from the solution and thus hampering the rate of the reaction initially. Particularly, Class F fly ash is prone to delaying the setting time, due to its low calcium content (Langan, Weng & Ward, 2002). Secondly, another aspect of the dilution effect is the fact that cementing particles are further dispersed when a SCM is added, causing the number of inter-particle bridges required to achieve a certain degree of hydration to increase. This, too, delays the reaction (Siddique, 2004).

It has been shown that the extent of the retardation of setting time is also dependent on the water/binder ratio. Particularly, the heat of hydration, which is a good indicator of the rate at which the cementitious reaction occurs, has been shown to decrease at water/binder ratios of 0.5 and above. This effect became less pronounced at water/binder ratios of 0.4 and less. The decrease in heat of hydration results in a decrease in the rate of reaction, thus implying a delay in the setting time (Langan *et al.*, 2002).

2.2.3.6 *Influence on compressive strength*

When considering the early age of concrete, fly ash in particular, and SCMs in general, affect the early age rate of strength gain and strength by means of three effects and phenomena: the filler effect, the previously mentioned dilution effect and the reactivity of the particular SCM. With regard to the magnitude of the final compressive strength, the level to which cement is replaced by an SCM, the fineness and type of SCM play equally important roles. Some of these factors are interconnected, as, for instance, the level to which cement is replaced is directly related to the dilution effect (Alexandre, 2016).

The filler effect describes the effect on the compressive strength that occurs during the filling of voids present in a concrete mix by smaller particles, such as those frequently present in fly ash. This decreases the total amount of voids and as such increases the early age strength of concrete. Therefore, the addition of fly ash can cause increases in compressive strength in this regard (Fennis, 2011).

The dilution effect has been described in Section 2.2.3.5. The addition of fly ash to concrete does not necessarily result in a diluting effect. When fly ash is added in order to substitute aggregate, a significant increase in early age compressive strength can be achieved (Papadakis, Antiohos & Tsimas, 2002; Oner, Akyuz & Yildiz, 2005). This is due to the fact that, effectively, a lower water/binder ratio is present when fly ash replaces aggregate, thus resulting in higher compressive strength. Furthermore, the finer particles provide more nucleation sites and therefore promote the hydration, and thus rate of strength gain, of the concrete. On the contrary, when fly ash is added to concrete in order to substitute cement, the dilution effect and impact of less reactivity can be observed (Siddique, 2007; Juenger & Siddique, 2015). Similarly to the negative effect on setting time, the dilution effect causes a decrease in early-age strength. This is due to the replacement of cement with less reactive fly ash, which causes the amount of hydration products, or calcium hydroxide, formed to decrease. Thus, the rate at which an alkaline environment is created decreases, which causes the pozzolanic reaction to not reach its full potential during early ages, as described in Section 2.2.1.3.

While the early-age strength might be influenced negatively by fly ash, it can often equal or exceed the strengths reached by conventional mixes at later ages (Papadakis *et al.*, 2002; Siddique, 2004; Oner *et al.*, 2005). Particularly at ages of 28 to 91 days it has been shown that mixes containing various types of fly ash exceeded the compressive strengths of conventional mixes. This is due to the pozzolanic reaction reaching its potential to a greater extent at these later ages, as more calcium hydroxide is produced over the longer period of time. The pozzolanic reaction utilizes this, as described in Section 2.2.1.3.

It must be noted that the type of fly ash also has an impact on the reactivity of fly ash and, thus, the strength reached (Siddique, 2004; Oner *et al.*, 2005). High calcium content fly ash has been shown to yield stronger concrete, while low calcium content fly ash results in lower strength concrete at early ages, but higher strength concrete at 91 days. Furthermore, fly ash with high lime contents shows high strengths at early ages but a slow strength gain.

As previously mentioned the level of cement replacement by fly ash has a significant impact on the performance of the concrete (Alexandre, 2016). Broadly speaking, up to a replacement level of 35% of cement, the resulting binder can be used in concrete intended for general construction work and as mass concrete. At replacement levels of more than 35%, the resulting binder can be used in concrete intended for use in structural fills, subbase and base courses and high-volume fly ash concrete. It thus becomes obvious that as the percentage of cement replacement increases, the strength of the resulting concrete decreases. It has however been argued that an optimum replacement level exists, which keeps the strength loss impact to a minimum. Up to this level, the strength difference between a standard reference mix and a mix in which cement has been replaced decreases, whereas at increasing replacement levels above this level the strength difference increases. Normally, the 28 day strength is taken as a reference as this is the strength used in designing of structures and is thus of the most practical value.

Furthermore, the optimum replacement level can be described as that point at which a state of optimum particle packing is reached in the mix (Oner *et al.*, 2005). The finer fly ash particles which are added to the mix mean that the overall surface area of the particles increases and voids in the mix decrease. This means that hydration products have more surface area to attach to due to the higher surface area, and more water available for hydration due to less water filling voids, thus resulting in improved strength and strength gain. However, above a certain replacement level, too many fines are present in the mix and the packing density is influenced negatively. Previously, a 25% replacement of cement by fly ash, or alternatively a 40% replacement of aggregate by fly ash, have been found to be the optimal replacement levels with regards to positive impacts on the compressive strengths of concrete (Bentz, Hansen & Guynn, 2011).

The final factor influencing the compressive strength of concrete containing fly ash is the fineness of the latter. In this regard it has been found that finer fly ash results in concrete with higher compressive strength (Chindaprasirt, Homwuttiwong & Sirivivatnanon, 2004). This can be explained by the higher reactivity of finer fly ash, which offers more surface area for hydration to occur. Furthermore the packing density is influenced positively by the finer and smoother particles, which leads to strength advantages over larger, coarser particles.

To summarise, Figure 2.5 shows the typical compressive strength development of concrete mixes with varying replacement levels of cement by fly ash, ranging from 0% to 35% of cement by mass (Alexandre, 2016). The figure illustrates the effect of later strength gain of fly ash mixes, as can be seen when comparing the 91 day strengths of the reference mix and fly ash mixes. Furthermore, with increasing replacement levels the differences in strength become greater, with higher replacement levels resulting in lower strengths. However, the highest replacement level of 35% still results in respectable compressive strength compared to a reference mix, especially at later ages.
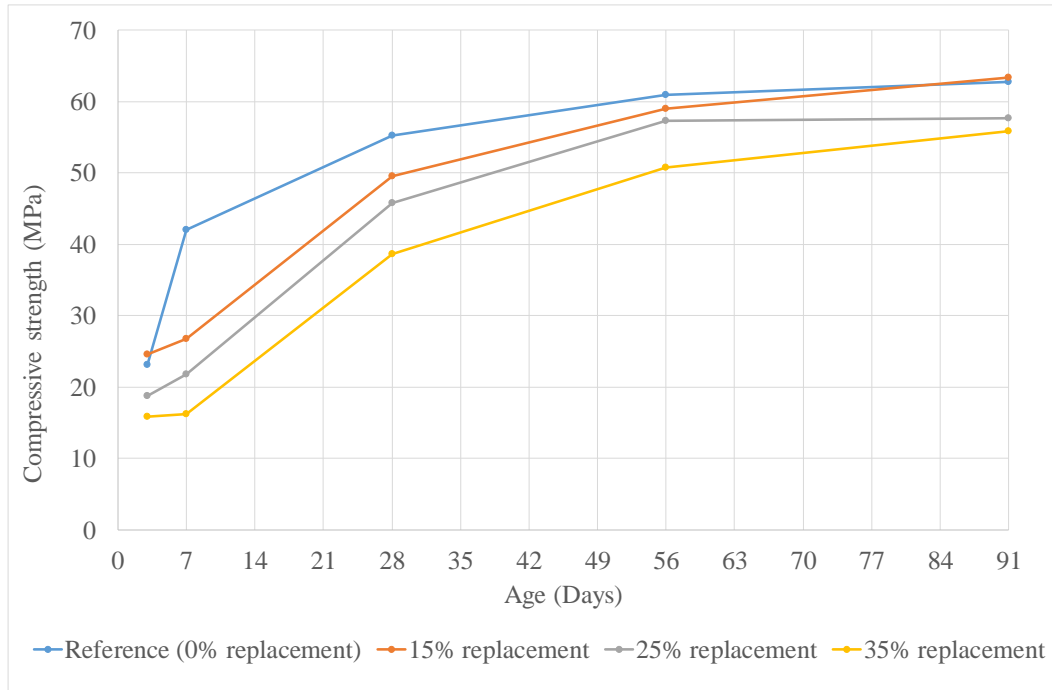
Figure 2.5: Typical compressive strength of mixes with various cement replacement levels by fly ash (Alexandre, 2016)

2.2.3.7 *Influence on durability*

With regard to durability, the impact of fly ash on permeability is of particular interest, as this is a mechanism with arguably the most adverse impact on the durability of concrete. Generally, it has been found that the inclusion of fly ash in concrete mixes has favourable impacts on the durability of concrete (Shi, Xie, Fortune & Gong, 2012; Zhang & Zhang, 2014). One of the principal reasons for this is the better distribution and shape of pores in concrete with fly ash content. This is caused by the finer fly ash particles causing a better dispersion of particles in the concrete mix, as mentioned during the discussion of particle packing. Due to this, the amount of critical pores is reduced, thus reducing the permeability of the concrete.

More specifically, the effect of an increased substitution of cement by fly ash has been noted to be a decrease in the permeability of the concrete. Class F fly ash has been shown to be more effective in reducing the permeability of concrete than Class C fly ash, most likely due to the higher calcium oxide content of the latter (Thomas & Matthews, 1992). It has also been shown that the higher the cement replacement level, the greater the decrease in permeability. However, this has only been found to be valid up to a cement replacement level of 50%, above which an increased permeability was again noted. At a replacement level of 50%, an 80% decrease in permeability has been noted (Dhir, El-Mohr & Dyer, 1997).

2.2.3.8   *Contribution towards embodied carbon content*

Since fly ash is considered a byproduct of the process of burning coal during electricity generation, it is widely assumed that it is a material that would be formed regardless of the demand for it by the concrete industry (Flower & Sanjayan, 2007). This implies that the greenhouse gas emissions that are considered for fly ash are those that take place after its production, i.e. after the burning of coal, which include the emissions during the capturing, refining, milling and transport of fly ash. As these emissions are insignificant when compared to the emissions occurring during the burning of coal, and the latter is ignored, fly ash has positive effects on the overall embodied carbon content of any concrete it forms part of (Cement and Concrete Institute, 2010). The concept of greenhouse gas emissions is further discussed in Section 2.5.2.

2.2.4   Ground limestone

2.2.4.1   *Definition of material*

Limestone is a sedimentary rock, which mostly consist of skeletal fragments of marine organisms. Widely spread and vast deposits of limestone occur, as it accounts for about 10% of all sedimentary rocks. It is mined and milled to form a fine powder, known as ground limestone. This inert substance is used as a filler in concrete, in order to improve the physical properties of the dry mix, ultimately resulting in concrete with improved fresh and hardened properties (Kronlöf, 1997).

Careful attention needs to be paid to whether limestone is used as a filler replacing cement or fine aggregate. The former is focused on in this section, as this is more compatible with the aim of this research.

2.2.4.2   *Chemical composition*

The main chemical components of limestone are calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$). However, several impurities can be present due to its geological history as a

sedimentary rock, the main ones being silica (SiO_2) and alumina (Al_2O_3). The typical chemical composition of ground limestone can be seen in Table 2.4.

Table 2.4: Typical chemical composition of ground limestone

Chemical component	Fraction (%)
$CaCO_3$	>40
$MgCO_3$	>30
SiO_2	7
Al_2O_3	<2
Fe_2O_3	<1

Ground limestone which is rich in calcium, and thus has a high $CaCO_3$ content, has been found to be effective in creating an alkaline environment (Nehdi, Mindess & Aitcin, 1996). This, in turn, is beneficial to the rate of the reaction, as mentioned in Section 2.2.1.2. Limestone of this nature is therefore especially effective in accelerating the rate of strength gain of concrete. Conversely, the above mentioned impurities are to be minimised, as they do not enhance the fresh or hardened properties of concrete (Grieve, 2009).

2.2.4.3   *Physical properties*

Physical properties of the ground limestone particles, such as particle shape and sizes, depend greatly on the grinding process used and are thus far-ranging. However, it can generally be assumed that limestone particles are of a round nature, as concluded in a study on five types of limestone fillers from various European sources (Diederich, Mouret, De Ryck, Ponchon & Escadeillas, 2012). The surface texture of the particles depends on the size class of the particles. Smaller limestone particles appear to be smoother than larger particles, this possibly due to the grinding process. This further explains the impact that the inclusion of particularly fine ground limestone filler has on workability and rheology.

2.2.4.4   *Influence on workability and rheology*

Different views exist on the influence of limestone on workability and rheology. On one hand, the use of inert fillers, such as limestone, has been shown to reduce the yield stress and plastic viscosity of the cement paste, due to the improved particle packing density of concrete when fillers are used (Ghezal & Khayat, 2002). The reduction of yield stress and plastic viscosity have been noted at cement replacement levels of up to 55%, with 80% of the filler passing the 0.075 mm sieve. This is possibly due to the fine nature and thus smooth particle texture of the limestone particles, as the effects were not found to be as pronounced for coarser limestone. Furthermore, the effects have been known to be most distinct at low cement levels.

2.2.4.5   *Influence on setting time*

Limestone has been found to have a positive impact on the setting time of concrete. Due to the effect of limestone particles acting as nucleation sites for calcium hydroxide particles present in the hydration reaction of concrete, the reaction is accelerated (Bonavetti *et al.*, 2003). Especially the hydration of C_3S is accelerated which, in turn, reduces the setting time of concrete. This effect is more pronounced for greater amounts and finer limestone fillers (Nehdi, 2000; Bosiljkov, 2003). However, it needs to be noted that this effect will occur when limestone is used as a sand replacement, or as a replacement for small quantities of cement.

2.2.4.6   *Influence on compressive strength of concrete*

The influence of ground limestone filler on the compressive strength of concrete needs to be differentiated into its influence on early age compressive strength and compressive strength at later ages.

It has previously been shown that the inclusion of limited quantities of ground limestone filler can have a positive impact on the early age strength of concrete. This is due to the previously mentioned effect of limestone particles acting as nucleation sites for the calcium hydroxide particles and products of the reactions of calcium oxide, silica and water, during the early stages of hydration. This accelerates the hydration reaction and provides greater initial strength gain (Nehdi *et al.*, 1996). It has been found that that this effect occurs up to a replacement level of 20% limestone by weight. Furthermore, the effect is most noted for ages up to 3 days, especially at replacement levels higher than 10% by weight of cement (Bonavetti *et al.*, 2003).

Different findings have been made with regard to the compressive strength at later ages when a limestone filler is included. Firstly, when limestone filler was purely used in increasing quantities in varying mixes, it was found that a substitution of cement by 50% limestone filler resulted in a 50% decrease in compressive strength, thus confirming the inert behavior of limestone (Menéndez, Triviño & Hernández, 1993). This can be seen in Figure 2.6. However, the selective use of limestone filler as a means of increasing the particle packing density of a concrete mix has resulted in mixes with equal or slightly superior compressive strength to a comparable mix without filler. In this regard, the fineness of the filler is also of importance. A finer filler, for instance limestone dust, resulted in superior compressive strength to a reference mix with the same cementitious content, as well as a mix with a limestone filler with larger particles (Saje, 2001; Bosiljkov, 2003). This is due to the larger total surface area the dust offers, which implies more nucleation and, subsequently, hydration. It has been established that a cement replacement level of circa 15 to 20% is optimal, as higher levels have

been shown to induce the previously mentioned strength loss (Palm, Proske, Rezvani, Hainer, Müller & Graubner, 2016).
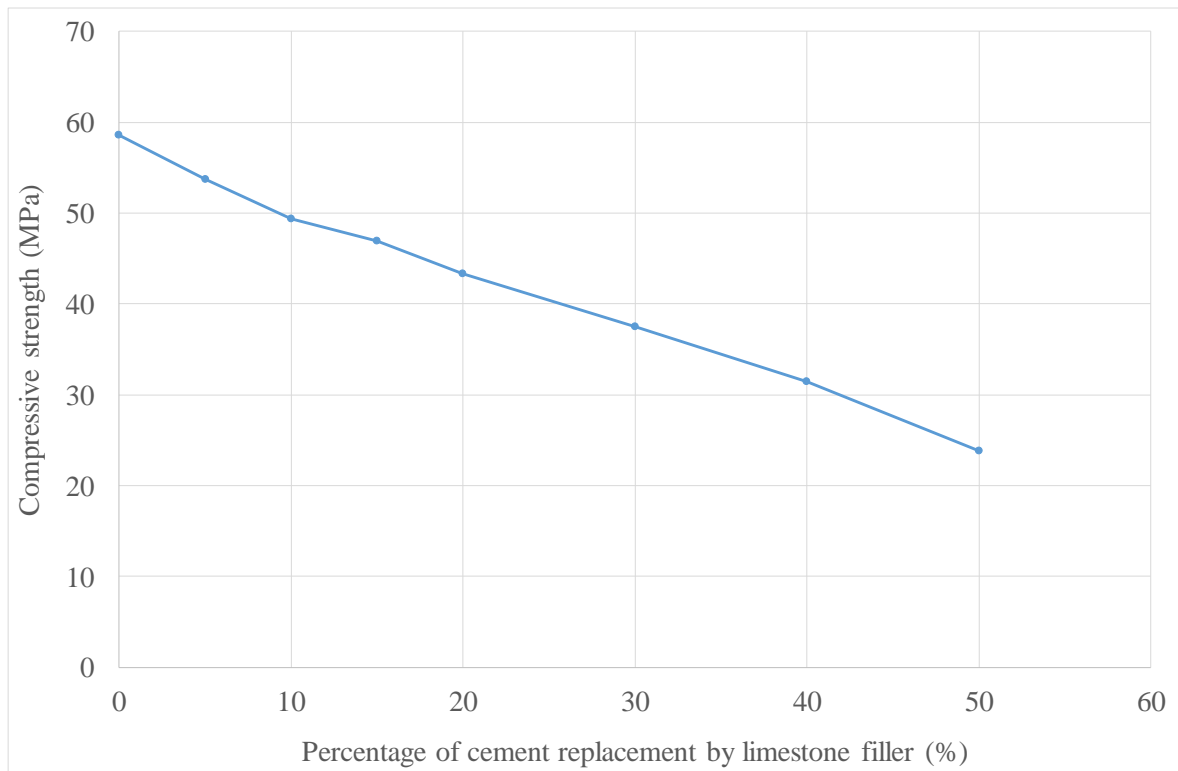
Figure 2.6: Compressive strength at 28 days age with varying cement replacement by limestone (Menéndez et al., 1993)

2.2.4.7   *Influence on durability*

To a great extent, ground limestone has a positive influence on the mentioned aspects of durability, namely permeability, absorptivity and diffusivity.

It has been found that the replacement of cement by up to 20% limestone by weight results in similar resistance to freeze-thaw attack of the resultant concrete as in similar concrete in which a conventional Portland cement was used (Klieger, 1985; Albeck & Sutej, 1991; Sprung, 1991). The freeze-thaw cycle is that cycle in which water in concrete pores expands in volume as it freezes and thus causes tensile stress in the concrete, which could exceed the concrete's capabilities and cause cracking. Concrete with low permeability is known to have a high resistance to this cycle and attack. It can thus be said that the inclusion of limestone does not have negative implications for the permeability of the concrete. It has, however, also been found that the quality of the limestone is of significant importance, as limestone which did not meet the standards set out in EN 197-1 (CEN,

2000) showed a relatively low resistance to freeze-thaw attack and thus lower permeability (Schmidt, 1992; Palm *et al.*, 2016).

Finally, the chloride diffusivity characteristics of Portland limestone cement has been shown to be dependent on the water/cement ratio (Palm *et al.*, 2016). At higher contents of limestone up to 45% by weight and water/cement ratios between 0.45 and 0.65, the diffusivity has been shown to increase. However, for a conventional replacement level of 20% by weight, a viable resistance against diffusivity is offered by Portland limestone cement compared to conventional Portland cement (Tsivilis, Batis, Chaniotakis, Grigoriadis & Theodossis, 2000; Dhir, Limbachiya, McCarthy & Chaipanich, 2007; Ramezanianpour, Kazemian, Sarvari & Ahmadi, 2012; Meddah, Lmbachiya & Dhir, 2014).

2.2.4.8   *Contribution towards the embodied carbon content*

The contribution of ground limestone towards the embodied carbon content is relatively small when compared to binders. For the latter, large amounts of energy are required during production, due to burning, for instance. As ground limestone only needs to be mined, refined, milled and transported, substantially less greenhouse gas is emitted before it forms part of a concrete mix. Its contribution to the embodied carbon content can be seen in Table 2.6 (Flower & Sanjayan, 2007; Proske *et al.*, 2014).

2.3   Superplasticiser

Superplasticisers can be defined as synthetic liquids which are soluble in water and have water-reducing capabilities, thus reducing the amount of water required for a concrete mix to reach a certain workability. Superplasticisers can thus be used to both lower the water and cement content, thus keeping the water/cement ratio constant and ensuring sufficient compressive strength (Cement and Concrete Institute, 1997). Generally, the mechanism by which this is achieved is the dispersion of cement particles within the mix. Modified acrylic polymer and polycarboxylate ether based superplasticisers are focused on as part of this study.

2.3.1   Types of superplasticiser and their plasticising mechanisms

2.3.1.1   *Polycarboxylate chemical base superplasticiser*

Polycarboxylate based superplasticisers are based on the polycarboxylate polymer, which consists of a backbone of carboxylic groups with polyoxyethylene side chains (Björnström & Chandra, 2003). This results in a molecule with a high molecular weight, which is beneficial towards the efficiency of its plasticising mechanism.

The plasticising mechanism of polycarboxylate is characterised by the absorption of the polymer by the cement particles (Uchikawa, 1994; Björnström & Chandra, 2003). This can be seen by the low

number of anionic groups formed during the reaction, indicating a low electrostatic repulsion of the type found in the reactions of conventional superplasticiser based on sulfonic polymers. This indicates that the polymers themselves are responsible for the dispersion effect, in a mechanism known as steric hindrance.

2.3.1.2   *Acrylic polymer base superplasticiser*

Contrary to conventional superplasticisers based on sulfonic polymers, such as lignosulfate and naphtalene, acrylic polymer superplasticisers are based on synthetic acrylic polymers. In many cases, these include chloride-free inorganic salts as a retarding admixtures, in order to prevent slump loss associated with conventional sulfonic superplasticisers (Collepardi, 1998).

Furthermore, similarly to polycarboxylate superplasticiser, the plasticising mechanism of acrylic polymer based superplasticisers differs from that of sulfonic superplasticiser. It has been found that relatively low numbers of negative anionic groups are found during the reactions of acrylic polymer based superplasticiser with cement, when compared to the reactions of sulfonic superplasticisers, which are based on the electrostatic repulsion of these anions (Tanaka, Matsuo, Ohta & Ueda, 2003). This indicates that the acrylic polymers are absorbed by the cement particles, and the polymer molecules themselves prevent the flocculation of the cement particles, thereby causing the dispersion of these particles and the plasticising effect on the concrete mixture. This is similar to the behavior observed in polycarboxylate superplasticisers, namely the mechanism of steric hindrance (Uchikawa, 1994). However, research shows that this mechanism is more pronounced in polycarboxylate superplasticisers, therefore giving it stronger cement dispersing capabilities. Additionally, the acrylic polymers line up linearly along the concrete flow direction, thereby further lubricating the mixture and increasing the plasticising effect (Collepardi, 1998).

2.3.2   Influence of superplasticiser on concrete

The influences of the superplasticiser on the properties of concrete can be far-ranging and are dependent on the purpose of the use of the superplasticiser in the particular concrete mix. More specifically, the three main purposes of the use of superplasticiser in a concrete mix could be in order to increase workability, reduce the water/cement ratio or reduce the water and cement content (Collepardi, 1998). These purposes and their effects on certain fresh and hardened properties are broadly illustrated in Figure 2.7, and are discussed in this section. In this study, and correspondingly this section, focus is laid on the latter purpose and its effect on concrete's properties.

Furthermore, in this context the effects of the two previously mentioned types of superplasticiser on these fresh and hardened properties are discussed.
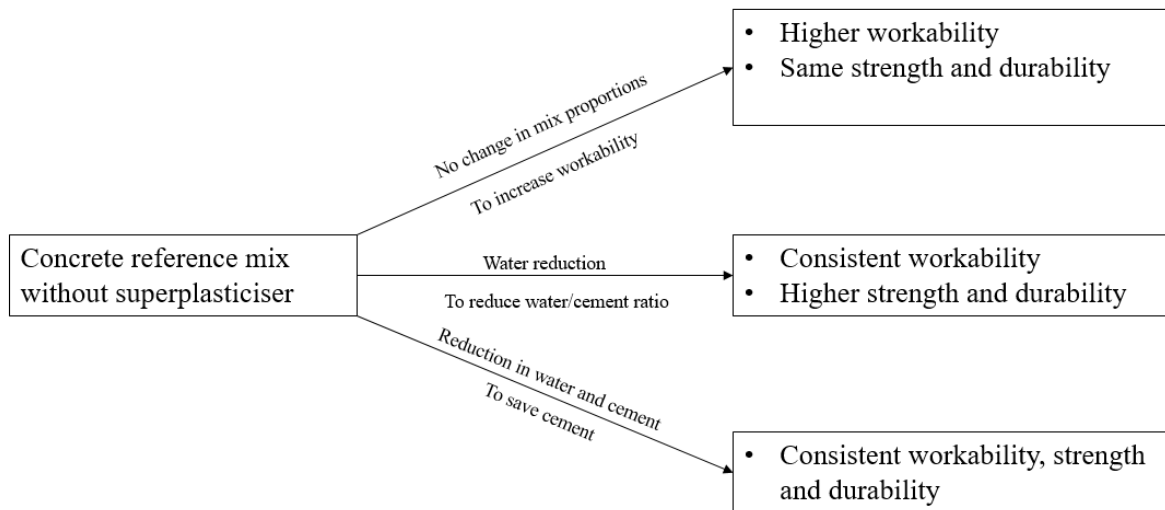
Figure 2.7: Applications of superplasticiser in concrete and effects of these (Collepardi, 1998)

2.3.2.1 *Influence on workability and rheology*

Regarding the rheology of concrete, generally, superplasticisers decrease the yield stress of concrete while increasing its plastic viscosity. This effect becomes especially pronounced at higher dosages of superplasticizer (Mork, 1996). This was confirmed for a PCE superplasticizer, which proved to decrease dynamic yield stresses at increasing dosages (Qian & De Schutter, 2018). For a cement paste a similar effect was observed: the yield stress was decreased while minimal decreases in plastic viscosity were observed (Ho, Sheinn, Ng & Tam, 2002).

However, it has been noted that this effect is dependent on the sand and cement content of the concrete (Tattersall, 2014). When added to a concrete mixture with a low sand content, namely a sand/aggregate ratio of 0.35, superplasticiser increases the viscosity. Conversely, at a higher sand/aggregate ratio of 0.45 the viscosity is decreased. The change in yield stress remained consistent, regardless of the sand content. Furthermore, the superplasticiser is more effective in reducing the yield stress of the concrete at higher cement contents.

Finally, it has been found that the acrylic polymer based superplasticiser is more effective than the polycarboxylate based superplasticiser in reducing the yield stress of the concrete mix. This can be attributed to the additional lining effect of the acrylic polymers, over and above the steric hindrance mechanism both superplasticisers posess (Collepardi, 1998). However, both superplasticisers have

been found to be more effective in reducing the yield stress of the concrete than the conventional sulfonate based superplasticisers (Björnström & Chandra, 2003).

2.3.2.2 *Influence on setting time*

Superplasticisers of any sort have been found to have a negative effect on the setting time, i.e. they delay the initial and final setting of concrete (Zhang, Sisomphon, Ng & Sun, 2010). This research shows that the heat of hydration of concrete mixes with sulfonic, polycarboxylate and acrylic polymer based superplasticisers reach their peaks at later stages when compared to reference mixes with only ordinary portland cement. In the case of the latter two superplasticisers, this has been attributed to the absorption of the superplasticiser by the cement particles, as the polymers on the surface of the cement grain form a boundary which hinders hydration reactions between cement grains and water.

When comparing the types of superplasticisers it can be seen that the polycarboxylate and acrylic polymer based superplasticisers do not delay the setting time to the extent that the sulfonic superplasticisers do (Zhang *et al.*, 2010). The former two superplasticisers display a greater heat of hydration at earlier times, when compared to the latter. Polycarboxylate based superplasticisers display an earlier setting time than acrylic polymer based superplasticisers, possibly due to the differing polymers providing varying boundaries between cement grains and thus delaying setting to varying degrees.

2.3.2.3 *Influence on compressive strength of concrete*

When evaluating the influence of superplasticiser on the compressive strength, the intended purpose of the use of superplasticiser is of primary importance. As mentioned, this study focusses on the use of superplasticiser in order to reduce the water and cement content, at a constant water/cement ratio.

The inclusion of an optimal dosage of superplasticiser in order to lower water and cement contents at a constant water/cement ratio does not have a negative impact on strength at early and later ages. Conversely, compared to a reference mix with 300 kg/m^3 cement, the compressive strength at 7 and 28 days of a mix with 270 kg/m^3 cement showed slight increases due to the inclusion of a superplasticizer (Hewlett, Edmeades & Holdworth, 1978). It has been hypothesized that this is due to the better dispersion of cement grains due to the superplasticiser, which is beneficial towards the hydration reaction at later ages, and thus aids the strength development. However, these slight strength gains are likely to be reversed when cement contents are decreased to levels at which the hydration reaction is significantly impaired. These levels differ, depending on the concrete mixture proportions (Mehta & Monteiro, 2006).

Furthermore, adding amounts of superplasticiser in excess of the optimal dosage can result in strength losses (Antoni, Halim, Kusuma & Hardjito, 2017). This could be due to the associated increase in segregation of the concrete, which is not beneficial towards the development of compressive strength. The optimal dosage can be found using established tests such as the flow table test (ANSI, 1969).

Finally, the use of polycarboxylate based superplasticisers results in higher compressive strengths of the concrete than can be achieved when using acrylic polymer and sulfonic based superplasticisers (Tkaczewska, 2014). Regarding the comparison with sulfonic based superplasticisers, this could again be attributed to the stronger cement grain dispersion capability of polycarboxylate superplasticisers. The differing types of polymers, namely polycarboxylate and acrylic, forming differing boundaries between cement grains result in an inferior strength and strength development of acrylic polymer based superplasticisers, when compared to polycarboxylate superplasticiser (Zhang *et al.*, 2010).

2.3.2.4 *Influence on durability*

It has been shown that a polycarboxylate superplasticiser has a positive impact on the durability of concrete, in terms of a decreased permeability when compared to a reference mix without superplasticizer (Toledano-Prados, Lorenzo-Pesqueira, González-Fonteboa & Seara-Paz, 2013). A decreased pore volume and average size, as well as porosity were noted, all of which contribute to a more dense structure of the concrete and less permeability. This is attributed to the improved interfacial transition zone when superplasticisers are included (Zhang & Kong, 2014).

Furthermore, polycarboxylate based superplasticisers reduce the water sorptivity and chloride permeability of concrete, and thus also have positive impacts on durability in these regards (Huang, Qian, Zhao, Qu, Guo & Danzinger, 2016). Research shows that more calcium silicate hydrate products were found when the polycarboxylate superplasticiser was included, and these products were homogenously distributed. Furthermore, these made water and chloride penetration more difficult and thus improved the durability.

When comparing the durability impacts of polycarboxylate and acrylic polymer based superplasticiser, the stronger cement dispersing capabilities of polycarboxylate superplasticiser again give it the advantage (Huang *et al.*, 2016). By dispersing the cement grains and calcium silicate hydrate products more homogenously, it provides more resistance to permeation, absorption and diffusion than the acrylic polymer based superplasticiser.

2.3.2.5   *Contribution towards embodied carbon content*

It has been established that the CO_2 emissions during the production of chemical admixtures such as superplasticisers are minor, as can be seen from Table 2.6. Furthermore, due to the small quantities in which these are used in a concrete mix, it has been suggested that their exclusion from calculations of the total embodied carbon content could be motivated, as their contribution towards this could be described as negligible (Flower & Sanjayan, 2007).

2.4   Particle packing density

As the creation of a low cement-content concrete entails a reduction of the water content in order to maintain a constant w/c ratio and compressive strength, workability of the concrete might be adversely effected. Optimal particle size distribution and packing density is a tool that could aid in mitigating the effect of a lower water content on the concretes workability (Proske *et al.*, 2014).

2.4.1   Definition of particle packing density

The distribution of particle sizes of a certain mix can be described as the fractions of various particle sizes that are present in a certain measure of that mix. The packing density of the particles can be defined as the way in which smaller particles fill the voids between larger particles (Cramer, Hall & Parry, 1995; Fennis, Walraven & Den Uijl, 2009; Moini, Flores-Vivian, Amirjanov & Sobolev, 2015). A mix with a high packing density would have a large share of voids between particles being filled by smaller particles, which results in a dense and stiff mix. Thus, a high packing density is an advantage when limited water is available in the mix. This is due to the limited volume of voids that are present and are thus not prone to being filled with water. Water can therefore almost exclusively be used to lubricate the particles in the mix, and thus improve the workability of the mix. Conversely, in a mix with a low packing density, more voids are present that are filled with water. This is illustrated in Figure 2.8.

| 100% cement | Cement + small particles | Cement + large particles |
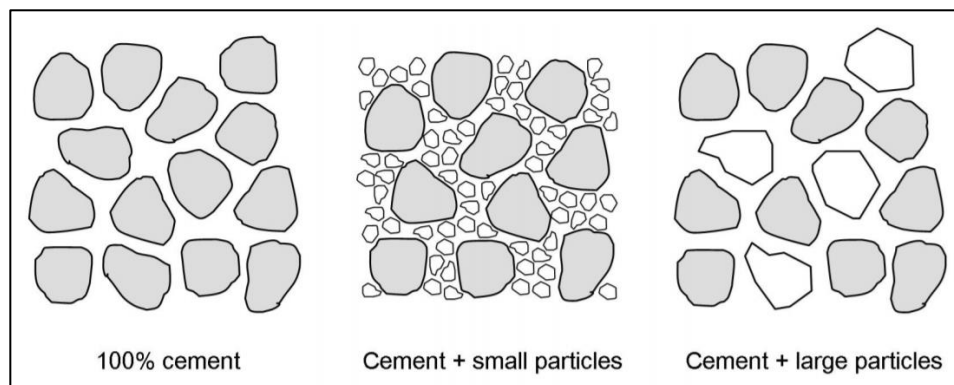
Figure 2.8: High packing density mix of cement with small particles and low packing density mix of cement with large particles (Fennis et al., 2009)

However, practically most mixes have a certain fraction of voids between the larger particles in the mix. These are mostly filled with cement paste during mixing, thus resulting in a denser, and therefore stiffer and stronger mix. Furthermore, space available for passage of water particles is decreased and friction between particles increases. This can have a negative impact on the workability of the mix. To counter this, excess cement paste is needed. In other words, cement paste not only needs to fill the voids between larger particles, but also be able to lubricate the mix and thus provide workability (Fennis, 2011).

Mathematically, packing density can be described as the ratio, α, of the volume of solid particles to the volume of the bulk mixture (Fennis, 2011). This is described by:

$$\alpha = \frac{V_p}{V_b} = \frac{\rho_p}{\rho_b}$$

(2.13)

with V_p being the volume of solid particles while V_b is that of the bulk mixture. It logically follows that the fraction of voids, ε, in the mix is given by:

$$\varepsilon = 1 - \alpha$$

(2.14)

Furthermore, dry packing density of particles can be established using:

$$\alpha = \frac{m_p}{\rho_p V_{container}}$$

(2.15)

with, m_p representing the mass of the particles, ρ_p representing their density and $V_{container}$ representing the volume of the container used for testing. Generally, the packing density of aggregate in concrete varies from 0.55 to 0.8 (Fennis, 2011).

It is therefore possible to obtain a mix with an optimal particle packing density. However, this particle packing density varies depending on the predominant particle shapes present in the aggregates (Fennis *et al.*, 2009). For instance, round sand particles interact differently with crushed rock aggregate than with rounded coarse aggregates. To estimate this difference and generally quantify the particle packing densities of various mixes, particle packing models are needed.

2.4.2   Properties of aggregate particles

This section describes various properties of aggregate particles, all of which have a direct influence on the overall packing density. These properties are of physical and chemical nature, and are influenced mostly by the origin as well as the history of the aggregate.

2.4.2.1 *Density*

The density of a material does not have a big influence on the particle packing density in general (Fennis, 2011). This is due to the fact that particle shape and size most likely govern when particles of similar density are mixed. However, when particles with highly varying densities are placed together, these might segregate due to heavier particles setting. This could have negative implications for the overall packing density of the mixture.

2.4.2.2 *Particle size and size distribution*

The size and size distribution of the particles significantly influences the overall packing density, especially for smaller particles with diameters less than 100 μm (German, 1989). These particles have a relatively low mass compared to their surface area, and this, in combination with a greater impact of interparticular forces, causes a decrease in packing density of the mixture, as particles repel and take up more volume.

However, as can be seen from Figure 2.8, the size of the particles has a positive influence on the packing density when the smaller particles fill the voids between the larger particles. This implies, that when aggregate particle sizes follow a uniform distribution, the wider the distribution, the better the packing density of the aggregate. Particularly, adding larger particles to a uniform distribution will increase the packing density as more volume is filled with particles (German, 1989). However, the type of distribution also influences the packing density to a large extent. When an excess amount of fine particles is present in the distribution, packing density is likely to decrease as the fine particles push the larger particles away and thus create new voids. This can be seen in Figure 2.9; a large amount of finer particles causes the larger particles to take up more space than before. Thus, more voids are created and packing density decreases (Fennis, 2011).
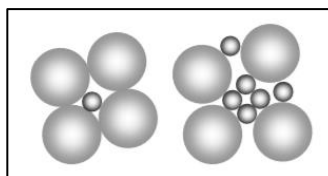
Figure 2.9: Influence of Particle Size on Packing Density (Fennis, 2011)

2.4.2.3 *Particle shape*

Generally, particle shape can be defined in terms of three properties, namely physical shape, surface texture and roundness (Barrett, 1980).

Physical shape refers to the size of the particle in all three dimensions (Fennis, 2011). For instance, particles can be flat or spherical. Physical shape can have a decisive impact on the packing density,

as it directly influences the size of the voids in the mix. Spherical particles have a positive impact on the packing density, whereas flat particles have a negative impact due to displacing other particles in one direction particularly and thus creating new voids (German, 1989; Kwan & Mora, 2002).

Surface texture is described as either being polished, smooth, rough or very rough (Fennis, 2011). A rougher surface texture influences the packing density in a negative way; namely, particles with a rougher surface texture will likely have miniscule interparticular voids, which decreases the packing density. On the contrary, a polished surface increases the packing density and workability of the mix, as less energy is required to compact the mixture. However, the strength of the concrete might be negatively affected by a polished surface, as the cement paste has a weaker connection to the particles (German, 1989; Kwan & Mora, 2002).

Roundness is described as either rounded, sub-rounded, angular or sub-angular (Fennis, 2011). In this regard, angular or sub-angular particles might have a negative influence on the packing density, as they tend to displace particles in one direction particularly, thus causing voids in the remaining directions. However, more angular shapes might have a positive impact during mixing, as they lessen segregation in the mix by locking particles in place. Generally, the packing density is not influenced negatively by the inclusion of more angular particles until these particles make out more than 10% of the mix. Furthermore, their interlocking ability adds strength to the concrete due to increased friction between particles (German, 1989; Kwan & Mora, 2002).

2.4.2.4   *Particle stability*

Another factor influencing the packing density of an aggregate mixture is the physical stability of the particles, and whether this stability can be maintained over the service life of the mixture. Particle stability is influenced by the durability properties, thermal properties and elasticity of the particles (Fennis, 2011). Durability refers to the degree to which the particles can resist any degradation, for example during a freeze-thaw cycle or crushing by an external force. If particles are degraded due to little durability, finer particles might form over time. This would change the structure and, thus, packing density of the mixture. Thermal properties of the particles are of importance as they determine the degree to which a certain particle might undergo physical change due to temperature fluctuation, and thus encounter degradation due to that physical change. As previously mentioned, this degradation to finer particles could result in a changed packing density. The elasticity of the particles is relevant as the change in particle shape associated with elastic behaviour can increase the packing density of the mix. However, it should also be noted that this elastic behaviour can result in less overall stiffness in the mixture.

2.4.2.5   *Chemical properties of particle*

With regard to the chemical properties of the aggregate particles, the chemical interaction between the aggregate and water used in concrete is of particular relevance (Fennis, 2011). In this regard, the adhesive properties of the particles are important. Adhesion refers to both the chemical and mechanical bond between a particle and liquid. The chemical bond can be due to the interaction between minerals in the aggregate and the liquid, whereas the mechanical bond depends on the physical properties of the particle. Surface texture and area play a particular role in the strength of the mechanical bond, with an increase in bond strength being noted for a rough surface texture. The stronger bonds in turn have an impact on the packing density of the aggregate mix. Namely, mixes with stronger bonds are likely to have an increased packing density, as the particles attract water to fill voids between them.

2.4.3   Forces acting on particles

The forces acting on the particles in a mix further influence the packing density of the mix. These forces can be of physical, electrostatical or steric nature, or Van Der Waals forces could be present (Fennis, 2011). Varying sizes and shapes of particles are affected by varying types of forces. For larger particles, physical forces have the largest influence on the overall packing density. For finer particles with diameters of less than 1mm, forces between particles become relevant. These forces could be of electrostatical or steric nature, or Van Der Waals forces could be present. The overall impact due to these forces is a decrease in packing density, as forces repel particles and cause these to take up more volume.

2.4.4   Particle packing density models

Since the 19th century, attention has been paid to practical ways in which the distribution of particles and their packing can be optimised. Before the advent of major computing power, most of this research was based on particle size distribution curves and optimisation curves. This work merely took the particle sizes into account and did not take note of the interaction between particles due to other forces, such as possible electrostatic forces (Andreasen, 1930). However, due to the relative simplicity of use of the grading curves, they are still being used in practice today and various codes such as the ASTM and European codes recommend their use. Particularly the Fuller curve is used extensively in this regard (Fennis, 2011; Moini *et al.*, 2015).

The next notable advance in the field was achieved by Powers, who took the interaction between components of concrete into account. This further gave rise to multiple component particle packing models, which include interaction between particles (De Larrard, Ledee, Sedran, Brochu & Ducassou, 2003). Several computer programs are based on the latter model, such as Europack,

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RENÉ-LCPC and 4C-Packing. Furthermore, due to the increasing power of computers, the discrete element modelling technique gained popularity. This entails modelling particles in 2D or 3D, and can additionally simulate non-spherical and flowing particles. The abovementioned techniques are discussed in further detail in the following sections.

2.4.4.1 *Optimisation curves*

With regard to particle packing models, optimisation curves can be described as the way in which groups of particles are combined so that the total particle size distribution is closest to the optimal mixture (Fennis, 2011).

The most famous of these curves is the Fuller curve, devised by Fuller and Thompson (Talbot & Richart, 1923). It is given by:

$$P(d) = \left(\frac{d}{d_{max}}\right)^{q}$$

(2.16)

with *P(d)* representing the percentage of aggregate of a certain size in the mix, *d* representing the particular diameter of the aggregate, d_{max} representing the maximum aggregate size limit and *q* representing an adjustment factor. For the Fuller curve this adjustment factor is taken as 0.5. The direct implications this has on the shape of the curve can be seen in Figure 2.10.
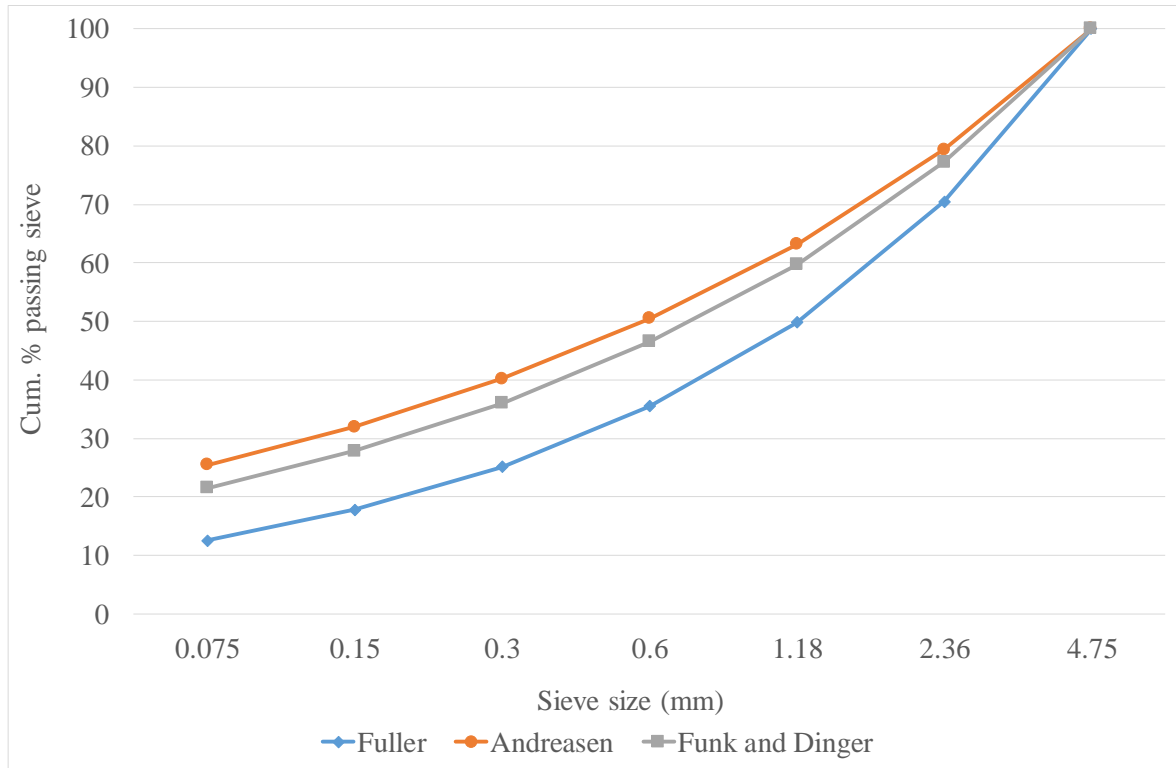
Figure 2.10: Particle size distribution according to various particle packing models

The Fuller curve has been optimised by various researchers. The methodology that was used to achieve this involved using varying values for *q*. For instance, a value of *q* in the range of 0.33 to 0.5 was suggested (Andreasen, 1930). Other research suggests using values of *q* that depend on the shape of the majority of particles present. For instance, it was suggested that a lower value of *q* be used for angular aggregates. When considering Equation 2.16 and Figure 2.10, where *q* was taken as 0.33 for the Andreasen curve, it can be seen that this implies that finer particles be added. This would allow for the voids between the angular particles to be filled and thus increase particle packing (Kumar & Santhanam, 2003).

The previously mentioned curves and investigations make use of a maximum aggregate size limit. In their research, (Funk & Dinger, 2013) concluded that a size distribution must also take the minimum aggregate size into account, in order to better represent the fine fraction of the aggregate. For this purpose, Equation 2.16 was modified resulting in:

$$P(d) = \frac{d^q - d_{min}{}^q}{d_{max}{}^q - d_{min}{}^q}$$

(2.17)

Funk and Dinger suggested an adjustment factor of 0.37 in this equation.

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These curves, however, fail to take into account the particle shape of the aggregate and assume that a higher packing density is achieved by merely using a wider range of particle sizes. However, in practice, the shape of the particles has a great influence on the overall packing density of the mixture, especially when the particle shapes vary significantly. It has been suggested that this should be accounted for by taking the adjustment factor as the average of all adjustment factors within each group of particle sizes (Zheng, Johnson & Reed, 1990).

Furthermore, a simplified grading distribution is assumed in each of the particle size fractions present in the grading curve (De Larrard, 1999). This assumption has an adverse effect on the accuracy of this model, as a variety of particle shapes and, albeit smaller range of particle sizes might be present within each of these fractions. Furthermore, a limited number of aggregate fractions is taken into account in these models.

As mentioned, optimisation curves have long been used due to their relative practicality. It has, however, also been argued that the degree of accuracy to which they take the grain size fractions, the processing method of packing and the particle shapes into account, is not sufficient. In order to make more accurate predictions, the compressible packing model was devised and is discussed in the following section.

2.4.4.2 *Compressible packing model*

The compressible packing model (CPM) is based on the linear packing density model for grain mixtures (Stovall, De Larrard & Buil, 1986), the former model being a more advanced version of the latter model. The CPM takes into account various factors regarding the particle shape, size, surface texture and the energy at which the dry mixture is compacted. The latter differentiates it from the linear packing density model (Fennis, 2011).

The CPM is based on the concept of a virtual packing density β, this being the highest possible packing density that a group of particles can achieve if they were to be placed individually, so as to take up the least space while keeping their original shape. For comparisons sake, the value of β of a group of identically sized spherical particles is 0.74, while the actual packing density in a random mix ranges from 0.60 to 0.64 (Cumberland & Crawford, 1987). This actual packing density is denoted by α. The actual and virtual packing densities of a monosized group of particles, α_j and β_j can be related by the applied compaction energy, K. Typical values for K for various methods of compaction can be seen in Table 2.5. The relationship is described by:

$$\alpha_j = \frac{\beta_j}{1 + \frac{1}{K}} \qquad (2.18)$$

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Table 2.5: Values of compaction energy for various compaction techniques (De Larrard, 1999)

	Technique	***K*-value**
Dry	Pouring	4.1
	Prodding with a rod	4.5
	Vibration	4.75
	Vibration and compression of 10kPa	9
Wet	Smooth thick paste (Sedran & Larrard, 2000)	6.7
	Proctor testing (Pouliot, Sedran, de Larrard & Marchand, 2001)	12
Virtual		Tends to ∞

For the more practical case of a mixture of particles with *n* size classes, class *i* being a dominant and *j* a less represented size class, the virtual packing density can be determined by:

$$\beta_{ti} = \frac{\beta_i}{1 - \sum_{j=1}^{i-1}[1 - \beta_i + b_{ij}\beta_i\left(1 - \frac{1}{\beta_j}\right)]r_j - \sum_{j=i+1}^{n}[1 - a_{ij}\frac{\beta_i}{\beta_j}]r_j} \qquad (2.19)$$

The virtual packing densities β_i and β_j can be determined using the actual packing densities α_i and α_j and Equation 2.18 (De Larrard, 1999). The variable r_j represents the volume fraction occupied by the particles of size class *j*. The variables a_{ij} and b_{ij} represent the loosening and wall effect respectively. The loosening effect describes the fact that smaller particles which are too large to fit between bigger particles push these apart and disperse them, thus decreasing the overall packing density. The wall effect describes the situation in which smaller particles in the vicinity of a larger particle or the wall of a container exhibit a lower packing density than that achieved in a pure mixture of these particles. a_{ij} and b_{ij} can be determined according to:

$$a_{ij} = \sqrt{1 - \left(1 - \frac{d_j}{d_i}\right)^{1.02}} \qquad (2.20)$$

$$b_{ij} = 1 - \left(1 - \frac{d_i}{dj}\right)^{1.50} \qquad (2.21)$$

These were determined by (De Larrard, 1999) using the CPM for binary granular mixtures. In these equations, d_i and d_j represent the diameters of particles of two size classes.

The real packing density α_t is determined by:

$$K = \sum_{i=1}^{n} K_n = \sum_{i=1}^{n} \frac{\dfrac{r_i}{\beta_i}}{\dfrac{1}{\alpha_t} - \dfrac{1}{\beta_{ti}}} \tag{2.22}$$

This relates the known values of the virtual packing density of the mixture (β_{ti},) the virtual packing density of the particular particle class i (β_i) and the compaction energy K for each of the n size classes that are present in the mixture, with α_t, which is solved for (Sedran & Larrard, 2000). The values of packing density and K can be determined for each size class, in order to finally determine the optimal mixture. This process requires more user experience than the previously mentioned method of optimisation curves. However, once this experience has been obtained, various computer packages are available for use, one of these being the BetonLabPro software (Fennis, 2011).

2.4.5 Influence of greater packing density on concrete

2.4.5.1 *Influence on workability and rheology*

A greater packing density, and all factors contributing to it, have positive implications on both the workability and rheology, which are by definition also interconnected (Koehler & Fowler, 2004).

As mentioned, the particle shape and texture are two of the factors which can influence packing density. A spherical shape and smoother texture of aggregate particles result in a greater packing density (Quiroga & Fowler, 2003). It was found that particles with such properties result in a concrete mix with a higher slump and, thus, lower yield stress than particles with elongated shapes and coarser textures. Particularly, it was found that spherical particle shapes result in lower viscosity in mixes, and that their impact on viscosity was greater than on yield stress (Tattersall, 2014). Furthermore, texture was found to have no significant impact on these aspects of concrete rheology.

The grading of aggregate in terms of particle size has a major impact on the packing density of the mixture, and as such on the workability and rheology of the concrete mix. In order to have a positive impact on the workability and rheology, all particle sizes, including those of cement grains, fine and coarse aggregate, should be taken into account during gradation. Increasing the size range is known to decrease the viscosity of the mix. Furthermore, uniform size distributions have been shown to decrease the water requirement of concrete for certain target slumps, and thus decrease the yield stress (Quiroga & Fowler, 2003). Contrary to this, mixtures in which certain size fractions were omitted and where the focus was only laid on achieving the maximum possible packing density have proven to be prone to segregation and requiring more water. It should therefore be aimed to achieve a balance

between a high packing density and a uniform gradation of aggregate, with a wide variety of particle sizes present.

2.4.5.2   *Influence on setting time*

To a large extent, setting times are decreased by an improved packing density (Fennis, 2011). However, this is only valid if cement is not replaced by an inert filler or supplementary cementitious material with undesirable properties. As previously mentioned, an improved packing density implies that less voids are present in the concrete, subsequently causing cement particles to be closer to each other. This causes bonds between them to be formed more rapidly, thus shortening the setting time of the concrete mix.

2.4.5.3   *Influence on compressive strength*

An improved packing density has a largely positive impact on the interparticular bonds and compressive strength, provided that cement is not replaced by less reactive materials and that cement content is not decreased drastically (Fennis, 2011). Due to less voids in the concrete, particles in general, and cement particles in particular, are closer to each other. As seen with regard to the setting time, this implies that hydration products have to bridge shorter distances, and leads to greater strength of the concrete.

2.4.5.4   *Influence on durability*

Theoretically, an improved packing density leads to a better durability of the concrete. This can be explained by the decrease in voids and pores in the concrete that is linked to a better packing density, and thus the elimination of a major transport mechanism leading to durability issues in concrete (Kronlöf, 1997; Fennis, 2011). For instance, it has been found that an improved packing density due to the addition of a filler to concrete can lead to increased resistance to freeze-thaw attack and a lower carbonation rate. However, when generally evaluating the durability of concrete mixes with improved packing density, it is important to look at the density and structure of the pores in the cement paste, as this does not necessarily have to be favourable with regard to durability, although these might lead to a higher packing density. To a greater extent, the water/binder ratio influences the durability behavior of these mixes. Therefore each mix needs to be evaluated individually, dependent on the types of materials used and proportions of the mix.

2.5   Determining sustainability of concrete during its lifecycle

In order to quantify the sustainability of concrete, the life cycle over which this property needs to be quantified needs to be defined and indicators for this property need to be obtained. For these purposes a note on life cycle analysis, and sustainability indicators of performance based nature can be helpful.

2.5.1   The lifecycle analysis of concrete

When analysing the sustainability of concrete it is important that, to the largest extent possible, the analysis covers the entire life cycle of the concrete. As concrete structures are often designed for a lifetime of 50 to 100 years, the environmental impact needs to be spread over this time (Müller, Breiner, Moffatt & Haist, 2014). It therefore needs to be kept in mind to not only aim for the biggest reduction in environmental impact of the concrete, such as the embodied carbon content, but to also increase the durability of the concrete. Unfortunately, sustainability indicators such as those discussed in Section 2.5.3 have not been widely used in connection with durability, as this would give an indication of both the immediate environmental footprint and the long term durability of the concrete, and as such encompass all aspects of sustainability. This, however, means that potential for future research exists.

2.5.2   Greenhouse Warming Potential

An aspect of sustainability is the amount of greenhouse gasses produced when creating a concrete mix, and aiming to reduce these to the greatest extent possible in order to ensure improved sustainability. A manner in which this can be quantified is by establishing the Greenhouse Warming Potential (GWP) of the mix. The GWP takes into account all gasses contributing to the greenhouse warming effect by using conversion factors to convert these to a common denominator, namely the equivalent carbon dioxide emission per kilogram of material (kg CO_{2e}/kg). GWP values have previously been calculated for each material in a conventional concrete mix, based on the energy consumed during their mining or production process, and during the transporting of the materials. The values of GWP are therefore not only dependent on the material but, for instance, on the region where they are produced, due to different energy production mixes and transport distances for different regions (Flower & Sanjayan, 2007; Cement and Concrete Institute, 2010; Proske *et al.*, 2014). Examples of sets of GWP values can be seen in Table 2.6, based on South African, European and Australian data respectively. Thus, if the quantities of the materials per cubic meter concrete produced and their GWP are known, the total GWP of the mix per cubic meter can be calculated by summing the contribution of each material. This value allows for a comparison between concrete mixes on the basis of their different total GWPs per volume of material.

Table 2.6: GWP (kg CO_{2e}/kg) associated with materials in a conventional concrete mix

Material	(Cement and Concrete Institute, 2010)	(Proske *et al.*, 2014)	(Flower & Sanjayan, 2007)
CEM I cement	0.818	0.8189	0.82
Fly ash	0.002	N.A.	0.027
Ground limestone	N.A.	0.0278	N.A.

Sand	0.005	0.0023	0.0139
Stone	0.005	0.0023	0.0459
Superplasticiser	0.220	0.7721	5.2×10^{-3}
Accelerator	0.220	N.A.	53×10^{-3}

N.A. = not available

2.5.3 Binder intensity and carbon dioxide intensity index

The binder intensity (bi) and carbon dioxide intensity (ci) index propose different, performance based manners in which the efficiency and, correspondingly, sustainability of concrete mixes can be established. In contrast to the previously mentioned value presented by the GWP, the bi index is not based on the unit of concrete volume but on any unit of functional performance, with compressive strength being the most widely used. For many applications of concrete, the bi index provides a more practical indication of the sustainability of the concrete, as the primary purpose of concrete in structural applications is mostly to provide strength, as taken into account by the bi index, and not merely volume, as taken into account by the GWP. The bi index thus has the advantage of making it possible to compare the efficiency and sustainability of binder use in concrete mixes with different performances, in order to establish the optimal mix (Damineli *et al.*, 2010).

The bi index can be quantified by:

$$bi = \frac{b}{p}$$

(2.23)

with *b* being the total mass of binder per cubic meter of the concrete mix (kg/m^3) and *p* being the functional performance requirement. This shows that the bi index can be defined as the mass of binder material needed to produce one unit of functional performance (Damineli *et al.*, 2010). As previously mentioned, the unit of functional performance would mostly be compressive strength, with 28 day strength being the most applicable due to its use in practice. However, this age, and the functional performance requirement, could be adjusted based on the application of the concrete, with previously used units including bending strength, modulus of elasticity and carbonation resistance, for instance.

The ci index is very similar to the bi index, with the only exception being that the total mass of binder *b* in Equation 2.23 is replaced, as can be seen by:

$$ci = \frac{c}{p}$$

(2.24)

with *c* being the total equivalent CO_2 emitted in order to produce one cubic meter of the concrete (kg CO_{2e}/m^3), i.e. the GWP established in Section 2.5.2, while *p* is still the previously mentioned unit of functional performance. *c* is established as discussed in Section 2.5.2 (Damineli *et al.*, 2010).

The bi and ci indices have various advantages over the traditional manner of calculating the total (equivalent) CO_2 emissions of the concrete. The two indices comprehensively assess the efficiency of binder use in concrete, and the CO_2 emissions due to this, and comparing this to any functional unit of particular interest. This assessment not only incorporates the selection of concrete materials, the efficiency in the production and the concrete mix design, but also the concrete mixing process by the use of, e.g. compressive strength as a functional unit. They thus offer a superior indicator of sustainability to the GWP.

2.6   Concluding summary

This chapter provides a literature review of several aspects relevant to this investigation. Firstly, background on concrete as a material and cement as one of its constituents is provided. It is noted that on average 842 kg of CO_2 are emitted during the production of cement, adversely impacting the sustainability of concrete as a construction material. However, the properties of concrete that have contributed to its success as a construction material are also highlighted and defined.

Subsequently, the use of supplementary cementitious materials (SCM) and fillers to replace cement is discussed. Advantages and disadvantages in terms of the effect this has on the properties of the concrete are discussed, amongst others the possibly negative effect on compressive strength and setting times, but positive effects on durability, workability and rheology. Furthermore, the positive effects that these materials could have on the embodied carbon content of concrete are pointed out.

Following this, the use of superplasticisers to reduce the water requirement, and subsequently cement content of concrete, is discussed. Different types of superplasticisers and their influence on various properties of concrete are pointed out. Amongst others, their possibly positive effects on compressive strength and durability are discussed, while the adverse effects on setting times are noted. Furthermore, the positive effect that superplasticisers could have on the embodied carbon content is noted.

Similarly, particle packing techniques used to reduce the water requirement, and subsequently cement content, are discussed. Their positive influence on compressive strength, workability and rheology, setting time and durability is discussed.

Finally, manners in which sustainability of concrete mixes can be established are discussed. As part of this the life cycle of concrete is discussed, and various indicators used to quantify sustainability are defined. It is seen that indicators based on functional performance could provide a more accurate indication of sustainability.

The literature reviewed confirms the need for an investigation into each of the manners of reducing the cement content, in order to investigate the effects of using South African materials and specific techniques, for instance. Furthermore little literature focusses on the interaction of the manners when they are used simultaneously. This provides further motivation for this research.

The next chapter provides the experimental framework of this study.

Chapter 3
Experimental Framework

This chapter presents the framework of the experimental investigations carried out as part of this study. Firstly, the methodology used to establish the optimally sustainable mixes is discussed broadly and, subsequently, more in depth for each of the approaches employed to achieve the ultimate goal. Thereafter, the materials used in this investigation and their specifications are discussed. Their physical and chemical properties are elaborated on subsequently. Following this, the mixing and casting procedure of the concrete is described, as well as the curing procedure. Finally, the testing procedures are elaborated on, including the testing procedures of the plastic, hardened as well as the sustainability properties of the concrete.

3.1 General methodology

The reduction of cement content in concrete can be achieved in numerous ways, with this investigation focussing on the inclusion of supplementary cementitious materials (SCM) and fillers as a cement replacement, inclusion of admixtures to lower cement content and particle packing to reduce the water, and subsequently, cement requirement. Due to the many ways in which these factors could interact and influence each other, it is vitally important to develop a procedure which is likely to result in the greatest reduction in cement content. A diagram laying out the general methodology of the investigation can be seen in Figure 3.1.
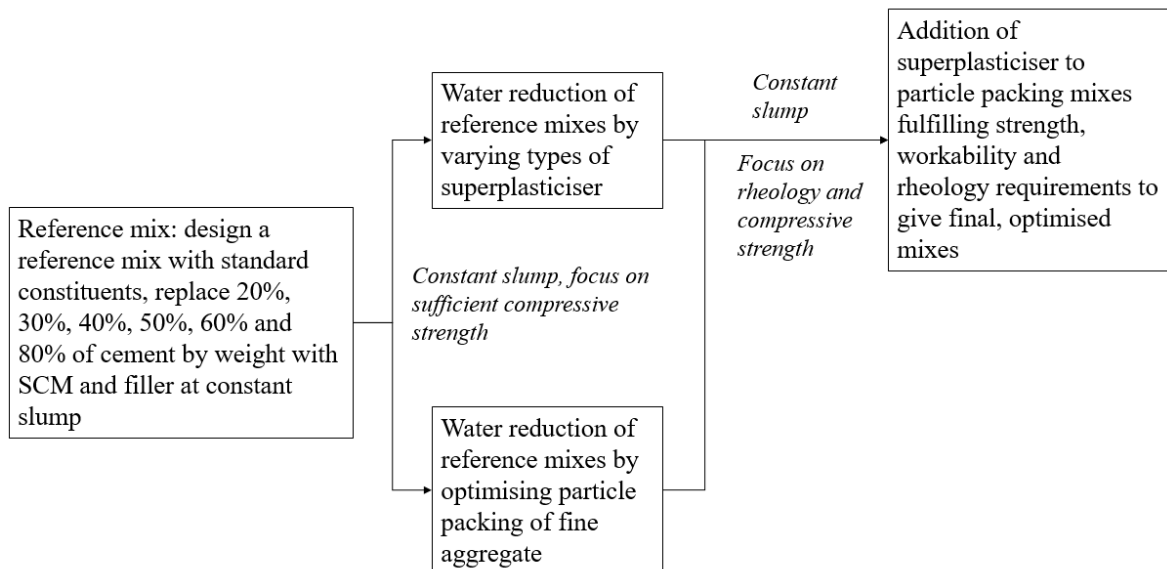
Figure 3.1: General methodology of investigation

As can be seen from the diagram, the first phase of the methodology involved developing a reference mix with a water/binder ratio of 0.5, a target slump of 100 mm and standard constituents, i.e. water, cement, fine and coarse aggregate. The C&CI mix design method was followed throughout the investigation (Addis & Goodman, 2009). The fraction of coarse aggregate per cubic meter of concrete was kept constant throughout the investigation, for all mixes developed. With regards to the cement content of the reference mix, 20%, 30%, 40%, 50%, 60% and 80% were replaced by SCM and fillers. This procedure is further described in Section 3.1.1. Following this, the water requirement of viable mixes established in the first phase was reduced by superplasticisers as well as optimised particle packing of the fine aggregate, separately, at the target slump and water/binder ratio previously mentioned. Viable mixes were selected based on compressive strength at early and later ages. This phase is further described in Sections 3.1.2 and 3.1.3. Finally, superplasticiser was added to viable mixes with optimised fine aggregate particle packing. Again, the previously mentioned water/binder ratio and slump were maintained. Viable mixes were again selected based on compressive strength, while additional emphasis was laid on the rheology of the mixes, particularly the influence of the superplasticiser, with mixes with excessive viscosity being eliminated. This final phase is further described in Section 3.1.4.

3.1.1   Mix design methodology of mixes containing SCM

In this first phase, fractions of the cement content of an established standard reference mix were replaced with a SCM and a filler, namely fly ash and ground limestone, respectively. These materials are elaborated on in Section 3.2.

The substitution of cement with SCM and filler took place while a constant water/binder ratio of 0.5 and a target slump of 100 mm was maintained. The methodology followed in this phase involved a 20%, 40%, 60% and 80% replacement of the cement content of the reference mix by weight, by fly ash, respectively. If the mixes showed sufficient compressive strength for measurement at early ages of up to 7 days, they were considered viable. Following this, half of the fraction of a particular mix replaced with fly ash was replaced by ground limestone. For example, in a mix where 20% of the cement was replaced by fly ash, 10% was replaced by ground limestone and 10% by fly ash. Furthermore, new mixes in which 30% and 50% of cement were replaced were developed. In these mixes, 20% or 30% were replaced by fly ash, respectively, and 10% or 20% by limestone. It could be argued that the aim of this was not to use the ground limestone as a filler in its original sense, i.e. in a way that improves the particle packing density, and therefore workability. This would have warranted a more scientific approach to the addition of ground limestone to the mix. More so, it was rather done to investigate the effects of the ground limestone on early-age strength and workability,

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both of which promised to be positive judging by the literature reviewed (Fennis, 2011). Again, a water/binder ratio of 0.5 was maintained and a slump of 100 mm aimed for.

3.1.2 Mix design methodology of mixes containing superplasticisers

Once the mixes described in Section 3.1.1 were established, two types of superplasticisers were used to lower the water requirement of these mixes. This, and the fact that a constant slump of 100 mm was again aimed for at a constant water/binder ratio of 0.5, made it possible to reduce the binder content. The types of superplasticiser used were a polycarboxylate (PCE) based and a modified acrylic polymer (MAP) based superplasticiser, which are further discussed in Section 3.2.5.1. For the cement in the reference mix as well as the SCM and cement combination of the other mixes in phase one, an optimal dosage of superplasticiser was established by means of the Marsh cone test. This test is further discussed in Section 3.3.4. Mixes for which this dosage was established and in which superplasticiser was subsequently used to establish new mixes with lower binder contents were selected based upon sufficient compressive strength.

Furthermore, in order to validate the results of the Marsh cone test, mixes with double the optimal dosage as determined by the Marsh cone test were developed. The results in terms of the rheological properties, setting time, compressive strength and durability were then compared to the mixes using the optimal dosage, to determine whether the optimal dosage can really be described as optimal. However, this was merely done as a confirmation of the Marsh cone test and these mixes were not used further.

3.1.3 Mix design methodology of mixes with optimised particle packing

In order to lower the water requirement of the mixes established in Section 3.1.1, the particle packing of their fine aggregate fractions was optimised. Particle packing was limited to the fine aggregate fraction as during the course of this investigation, this was found to have the largest impact on the water requirement of the concrete mix. Furthermore, to bridge the gap in particle sizes between fine and coarse aggregate proved to be practically challenging in terms of the availability of aggregate with the required sizes. To achieve the optimal particle packing, the Fuller curve in combination with the Funk and Dinger equation was used, as discussed in Section 2.4.4.1 and particularly Equation 2.17. This yielded the optimal size distribution of the fine aggregate particles, according to which the fine aggregate fractions of the mixes were then graded by sieving the sand and combining the various sizes so that the distribution provided by the equation was matched. Subsequently, as a slump of 100 mm was again aimed for and the water requirement had effectively been reduced, the binder content of the mixes could also be reduced. The mixes for which this was performed were selected based upon sufficient compressive strength for measurement.

3.1.4   Mix design methodology of optimal mixes

Finally, all procedures of reducing the binder content of concrete were combined in order to present the greatest possible reduction. The resulting mixes were deemed to be the "optimised mixes", with the term "optimised" referring to the binder content of the mixes. The most practical way of achieving this was found to be the addition of superplasticisers to the mixes with varying cement replacement levels and optimised fine aggregate particle packing, i.e. those mentioned in Section 3.1.3, at a constant slump of 100 mm and water/binder ratio of 0.5. The mixes to be optimised were again selected based on sufficient compressive strength. However, for this final step emphasis was also laid on rheological properties of the concrete, and particularly the impact of superplasticisers. The dosage of superplasticiser that was added to the respective mixes was the dosage determined for the respective cement and SCM combination of the respective mix, as previously determined using the Marsh cone test.

3.2   Materials

3.2.1   Water

During the course of the investigation municipal tap water was used as mixing water. The same source of water was used throughout.

3.2.2   Binders and filler

A CEM I 52.5N Portland cement was used throughout the investigation as supplied by Pretoria Portland Cement (PPC). This cement is free of any additives such as fly ash or limestone, but contains gypsum. It has an ordinary rate of hardening and a 52.5MPa strength class.

Two types of fly ash were used during initial trial mixes, supplied by Ulula Ash and Durapozz, respectively. However, due to the superior impacts on workability of the latter, it was decided to use it throughout the investigation.

As a filler, a local ground limestone known by the commercial name Filla 15 was used throughout the investigation. This limestone originates from the vicinity of Vredendal, South Africa.

The chemical and physical properties of these materials are discussed in Section 3.3.

3.2.3   Aggregates

Certain fine and coarse aggregates were used throughout the investigation. The term fine aggregate refers to the sand used, and can also be described as that part of the aggregate of which more than 90% by mass passes the 4.75 mm size sieve. Sands locally known as Malmesbury sands were used throughout this investigation. Specifically, a coarser and finer Malmesbury sand were used in order

to have a large range of particle sizes. These sands form during the disintegration of rock and occur in the Western Cape area of South Africa. Throughout this investigation, a 50/50 blend of fine and coarse Malmesbury sand was used, i.e. the required fine aggregate fraction was split in two between these two sands.

The term coarse aggregate refers to the stone used, and can also be described as that part of the aggregate of which more than 90% by mass is retained on the 4.75 mm size sieve. Locally available Greywacke stone with a nominal diameter of 19 mm was used throughout this investigation. This was produced by crushing Malmesbury shale in the Western Cape area of South Africa. Some of the properties of the sand and the stone can be seen in Table 3.1.

Table 3.1: Properties of fine and coarse aggregate

	Fineness modulus	Relative density
Fine Malmesbury sand	1.162	2.62
Coarse Malmesbury sand	1.718	2.62
Greywacke stone	-	2.8

3.2.4   Admixtures

Two types of superplasticiser were used as admixtures during the course of this investigation, namely a superplasticiser based on polycarboxylate (PCE) and a superplasticiser based on modified acrylic polymer (MAP). The former has the commercial name Premia 196 and the latter Dynamon SP1. They were supplied by Chryso SA (Pty) Ltd and Mapei South Africa (Pty) Ltd respectively. Their specifications can be seen in Table 3.2. It must be noted that the recommended dosages are valuable guidelines provided by the manufacturers above which the superplasticiser is likely to have adverse effects on the concrete. Therefore, within these guidelines optimal dosages for the superplasticisers were established, as discussed in Section 3.3.4.

In order to minimise the delay in setting time, a lesser aspect of this investigation included the use of an accelerating admixture. In this regard, an accelerator with the commercial name Xel 650 was used. This was supplied by Chryso SA (Pty) Ltd. Its specifications can be seen in Table 3.2.

Table 3.2: Specifications of chemical admixtures

Commercial name	Relative density	Recommended dosage (%)*
Chryso Premia 196	1.055	0.3-3
Mapei Dynamon SP1	1.08	0.6-1.2
Chryso Xel 650	1.45	0.4-2.5

*by supplier, as % of binder weight

3.3   Tests of material properties

3.3.1   Particle size distribution

The particle size distributions of all fine aggregate, as well as the cement, fly ash and ground limestone used in this investigation were determined. For the fine aggregate, the procedure set out in SANS 201:2008 (SANS, 2008) was followed. The results of this can be seen in Figure 3.2. The particle sizes of the finer cement, fly ash and ground limestone were tested by means of the light scattering analysis technique. The results of this can be seen in Figure 3.3.

As indicated by the supplier, the coarse sand was found have greater fractions of larger particles than the fine sand. This is especially evident in the size range from 0.3 to 0.6 mm. However, the coarser sand also contains a larger fraction of dust than the fine sand, indicated by the higher percentage of particles with sizes between 0 and 0.075 mm. This could increase the water requirement of the concrete and thus prove unfavourable towards the reduction of cement content when merely the coarse sand is used.
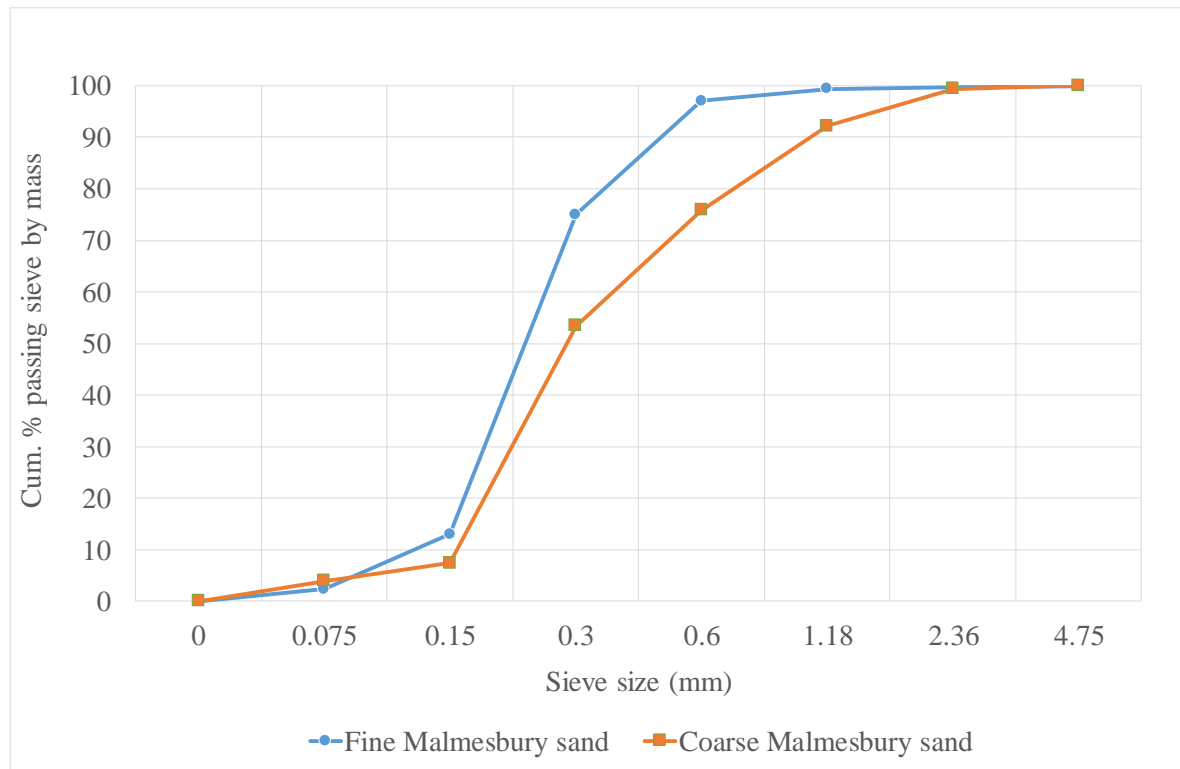
Figure 3.2: Particle size distribution of fine aggregates

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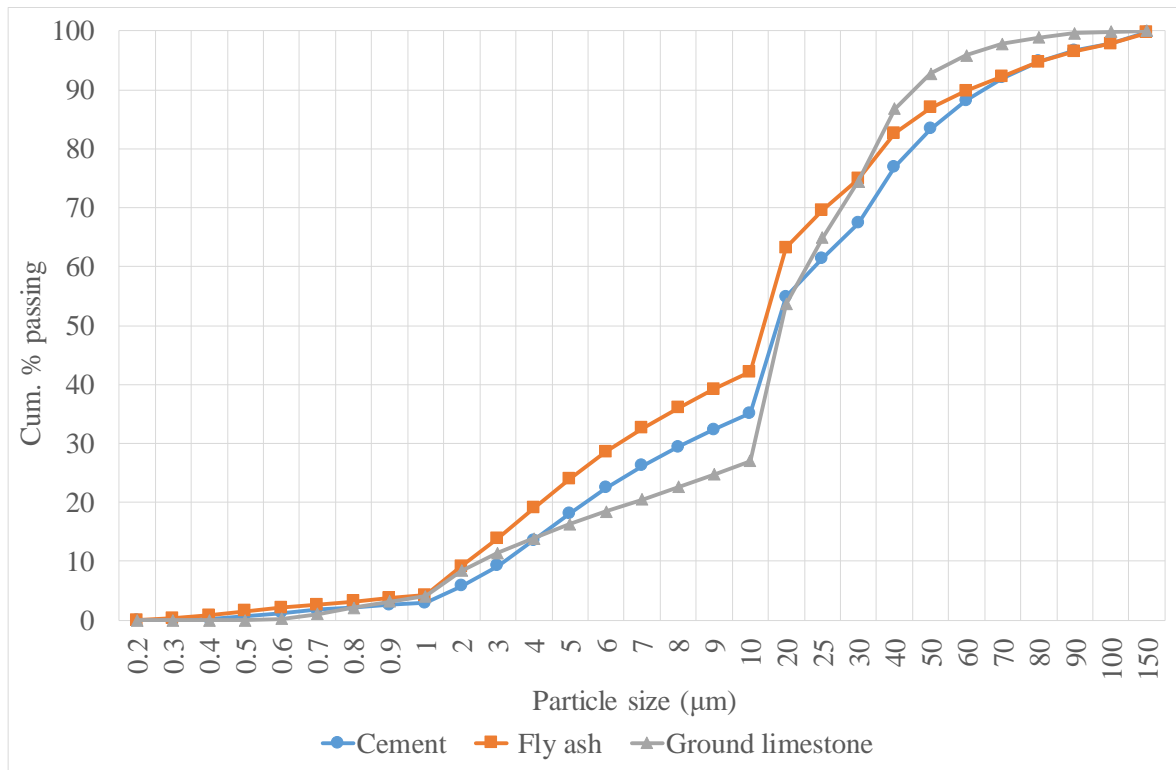
Figure 3.3: Particle size distribution of cement, fly ash and ground limestone

3.3.2   Chemical analysis

In order to determine the chemical composition of the cement, fly ash and ground limestone used, an X-ray fluorescence (XRF) analyses were conducted. These results make it possible to classify the materials and possibly explain their behaviour in a concrete mix, e.g. strength development. Furthermore, the loss on ignition (LOI) was conducted. During the test, the sample is heated to a predetermined temperature, which causes volatile substances to ignite and escape. This is done until the mass of the sample no longer changes, at which point it can be determined how much mass of the sample was "lost to ignition". The results of the XRF analyses and the LOI test can be seen in Table 3.3.

The chemical composition of the fly ash reveals that it is a Class F fly ash, as most South African fly ash. It can be seen that the ground limestone has a high CaO content. It would thus be effective in creating an alkaline environment, which should be beneficial towards the strength development of a mix containing ground limestone.

Table 3.3: Chemical composition of cement, fly ash and ground limestone used

	Cement (%)	Fly ash (%)	Ground limestone (%)
Al_2O_3	4.23	32.54	3.12
CaO	66.98	4.58	27.02
Cr_2O_3	0.01	0.03	-
Fe_2O_3	3.14	3.17	0.73
K_2O	0.55	0.67	1.10
MgO	0.95	0.98	19.81
MnO	0.07	0.03	0.02
Na_2O	0.27	0.22	0.11
P_2O_5	0.13	0.47	0.05
SiO_2	19.92	54.76	7.56
TiO_2	0.25	1.64	0.15
Loss on ignition	2.51	0.51	41.28

3.3.3   Marsh cone test

The Marsh cone test was conducted according to ASTM C939-10 (ASTM, 2010). As part of this, mortar mix designs were developed which can be seen in Table 3.4. As the purpose of this test was to investigate the interaction between superplasticisers and cement or cement/binder combinations, while also accurately simulating the reference mix designs, the mortar mix designs were based on the reference mix designs. This implies that the same binder/sand ratios were used in the mortar mix designs as in the reference mix designs, for each of the cement or cement/binder combinations. The test was conducted on those mixes that were deemed to be plausible for further investigation, e.g. that showed sufficient compressive strength.

Table 3.4: Mortar mix designs for Marsh cone

Mix*	REF	FA20	FA40	FA60
Water (kg/m³)	344	320	300.8	280
Cement (kg/m³)	688	512	360.96	224
Fly ash (kg/m³)	0	128	240.64	336
Fine sand (kg/m³)	572.33	604.29	628.3	658.37
Coarse sand (kg/m³)	572.33	604.29	628.3	658.37
Real binder/sand ratio	0.60	0.53	0.48	0.43
Mortar binder sand ratio	0.60	0.53	0.47	0.43

*Refer to Section 3.4.4 for terminology of mixes

Once the mix designs were established, the mortars were mixed as described in Section 3.4.1.2, with the inclusion of superplasticiser at the minimum dosage recommended by the manufacturer, by weight of binder. Immediately after mixing, the Marsh cone, which can be seen in Figure 3.4, was filled with the mortar to the prescribed level as the bottom opening of the cone was held closed. Once the cone was filled, the opening was opened and the time taken for the cone to empty measured to

the nearest second. This procedure was repeated for various dosages of superplasticiser at increments of 0.1% of binder weight, for each cement or cement/binder combination, as well as two types of superplasticiser, pointed out in Section 3.2.5.1. The results of this can be seen in Figure 3.5 and Figure 3.6. It can be seen that the time taken for the mortar to flow through the Marsh cone decreases the higher the superplasticiser dosage, up to a certain dosage. At dosages higher than this, the time taken to flow through the cone stabilises and no significant decreases in flow time occur. It can thus be said that this dosage represents the optimal dosage of superplasticiser. The optimal dosages are given in Table 3.5.
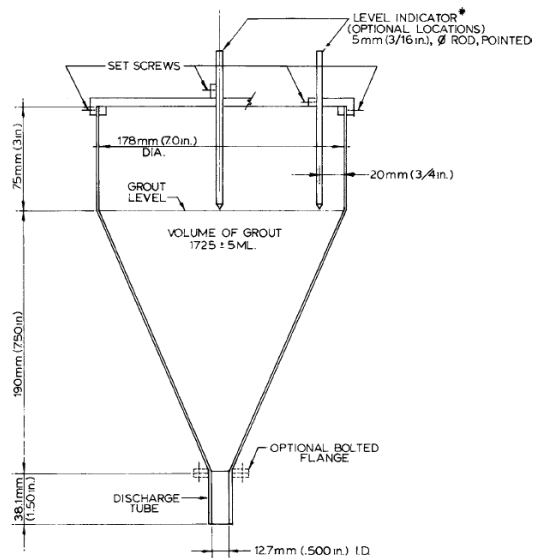
Figure 3.4: Cross-section of Marsh cone (ASTM, 2010)

Table 3.5: Optimal dosages of superplasticisers determined by Marsh cone test

Cement/binder combination*	REF	FA20	FA40	FA60
PCE superplasticiser (PCE) (%)	0.9	0.7	0.6	0.8
Acrylic superplasticiser (MAP) (%)	1	0.6	0.5	0.6

*Refer to Section 3.4.4 for terminology of mixes

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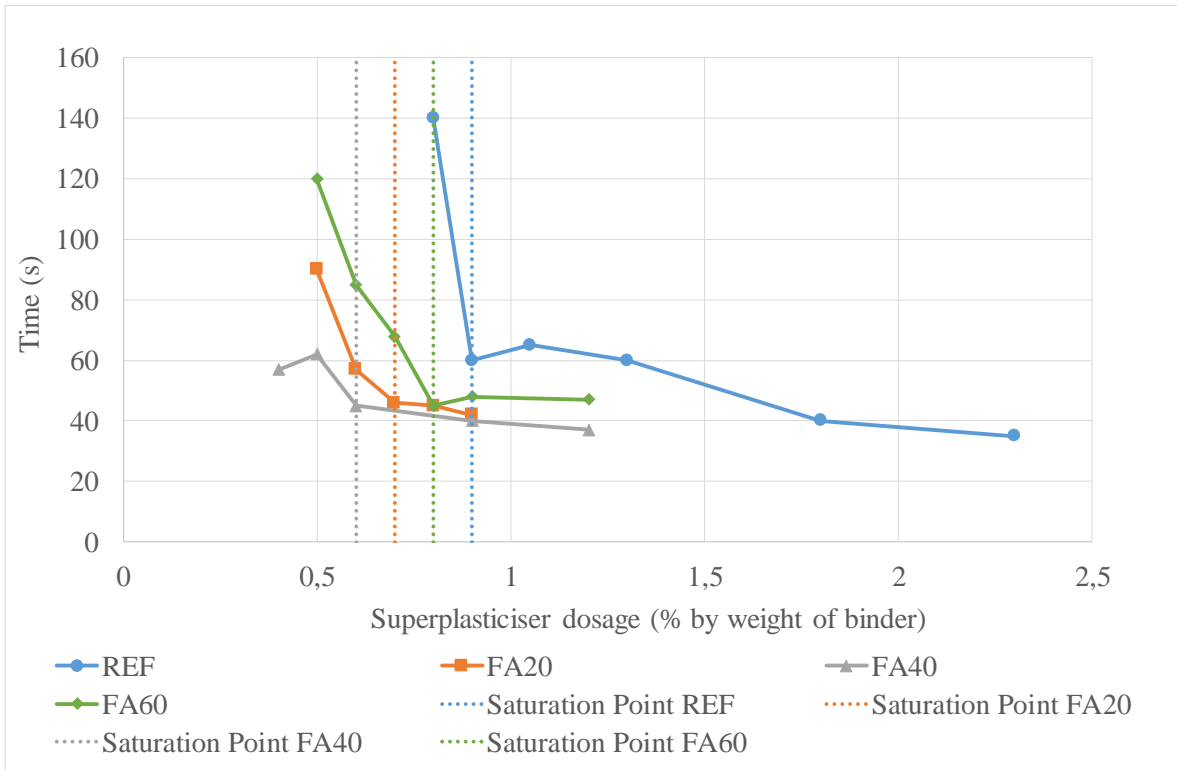
Figure 3.5: Results of Marsh cone test for PCE based superplasticiser
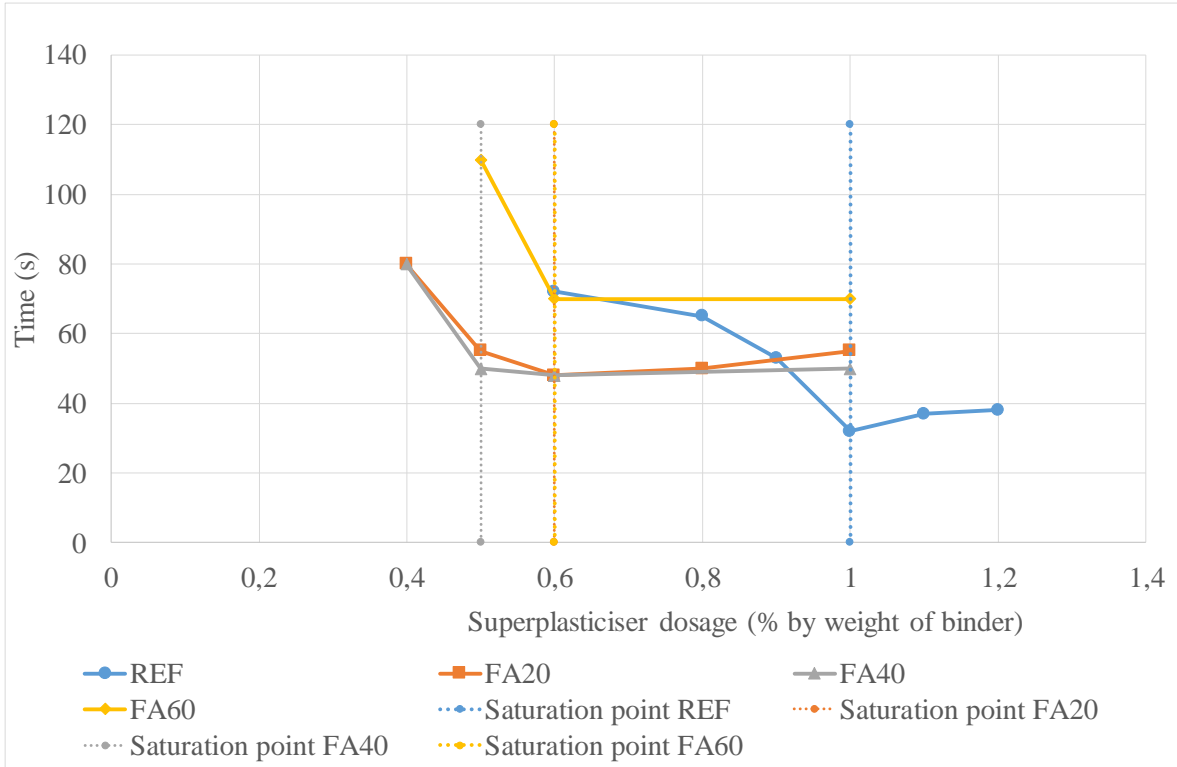
Figure 3.6: Results of Marsh cone test for MAP based superplasticiser

For both superplasticisers it can be seen that up to a replacement level of 40%, i.e. Mix FA40, the optimal dosage decreases, after which a slight increase for a replacement level of 60% is seen. This thus implies that as the cement content is decreased, less superplasticiser is needed to show significant reductions in flow time. Furthermore, as all mixes did not flow at low or no superplasticiser dosages, this can not only be due to the positive impact of fly ash on workability. Hypothetically, as less superplasticiser is needed to saturate the mixes at lower cement contents, this could indicate a greater interaction of the superplasticiser with the cement than with the fly ash.

3.4   Pre-experimental procedures

3.4.1   Mixing procedure

As some tests required only a mortar and others concrete, both of these needed to be mixed at certain stages of the investigation. Different procedures were followed for the two and these are laid out in the following sections.

3.4.1.1   *Concrete*

The materials needed for each mix were weighed off to the nearest gram prior to mixing. The mixing itself took place using rotary pan mixers with capacities of 0.025 and 0.05 m^3 respectively. Mixes with a maximum volume of 0.02 m^3 were mixed in the smaller mixer, while the larger mixer was used for mixes with a maximum volume of 0.04 m^3.

Immediately before mixing commenced the mixing pan and mixer blades were wetted and dried with tissue paper so that these were saturated to the same extent for all mixes. Sand, fly ash, ground limestone, cement and stone were then added to the mixing pan in the aforementioned order, for mixes in which all of these materials were added. The order was kept for mixes in which some of these materials were omitted, e.g. cement was always added after fly ash. After this the mixer was starter. Dry mixing of the materials then took place for the first 25 seconds, before the mixing water was added. In the cases where admixtures were added, these were added to the mixing water before the addition of this to the mix. The total mixing time from starting to switching off the mixer was 4 minutes, for all mixes.

3.4.1.2   *Mortar*

The materials needed for each mix were weighed off to the nearest gram prior to mixing. A smaller, "cake mixer" with a capacity of 0.005 m^3 was used to prepare the mortar mixes. The maximum volume of the mixes that were prepared was 0.004 m^3.

Before mixing began, the blades and bowl of the mixer were again saturated with water, and dried with tissue paper. Sand, fly ash and cement were added to the bowl in the aforementioned order before mixing. The procedure of the mixing process can be seen in Table 3.6.

Table 3.6: Mixing procedure for mortars

Step	Time (s)	Mixing speed
Dry mixing of materials	0-30	1
Add water	30-60	1
Add admixtures	60-90	1
Mixing	90-150	1
Mixing	150-330	2
Stop and scrape materials from sides	330-390	-
Mixing	390-570	2

Directly after mixing, the bowl was emptied and the mortar used for the particular tests.

3.4.2   Casting procedure

The moulds used to cast concrete cubes for compressive strength and the Oxygen Permeability Index (OPI) tests have side lengths of 100 mm. The same casting procedures were used throughout the investigation, with the moulds being filled and the same vibrating table used to consolidate the samples throughout.

After mixing, concrete was poured into the moulds so that these were filled to a height of approximately 50 mm. Vibration then took place for a duration of 30 seconds before the moulds were filled completely, to a height of 100 mm. The moulds were further vibrated until the expulsion of air bubbles to the surface slowed down significantly, at which point it was assumed that full compaction of the concrete has been achieved. This resulted in a total compaction time of no longer than approximately 3 minutes for the mixes. Different casting procedures were followed when the setting time test was conducted. These procedures are described in Section 3.5.3.

3.4.3   Curing procedure

Immediately after compaction, the moulds were placed in a climate controlled room. The temperature in this room was 25°C while the relative humidity was 65%. After 24 hours in this room, the cubes were demoulded and placed in curing tanks filled with lime saturated water, with a temperature of 25°C. The cubes were cured in the tanks until their day of testing.

3.4.4   Terminology of mixes

In order to quickly identify mixes, nomenclature was developed, which made it possible to deduce the fraction of cement in a mix that had been replaced by fly ash or ground limestone, if

superplasticiser of optimised particle packing had been used to reduce its water requirement, and which type of superplasticiser had been used. Figure 3.7 clarifies the terminology used to describe mixes throughout this investigation by giving an example of an applicable mix.

FA10GL10-PP-MAP

| FA10 indicates a 10% replacement of cement by fly ash | GL10 indicates a 10% replacement of cement by ground limestone | PP indicates optimised fine aggregate particle packing in the mix | MAP indicates an acrylic polymer based superplasticiser, PCE would indicate a PCE based superplasticiser, ACC would indicate an accelerator |
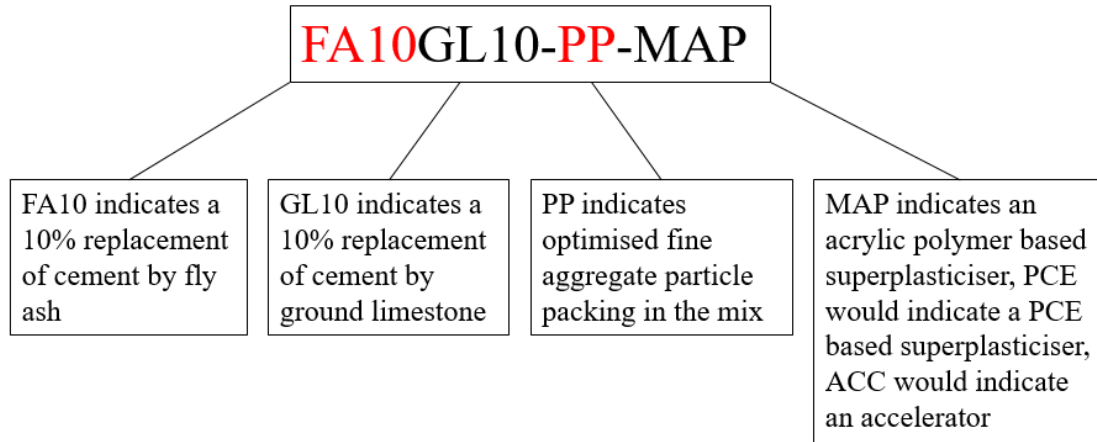
Figure 3.7: Nomenclature of mixes

3.5   Tests for plastic properties

Tests were conducted on the concrete in its fresh, plastic state. These tests took place according to the relevant standards and are described in the following sections.

3.5.1   Slump test

The slump test was carried out in order to determine the workability of the concrete. It was carried out according to SANS 5862-1 (SANS, 2006b), with the prescribed slump cone, base plate and tamping rod as equipment. These can be seen in Figure 3.8. Firstly, it was assured that the slump cone and base plate were clean and slightly moistened. Thereafter, while downward pressure was applied to the slump cone, it was filled with the freshly mixed concrete so that approximately a third of the cones volume was filled at a time, layer by layer. After each of these layers, 25 strokes of the tamping rod were applied to their surfaces, ensuring that the tamping strokes penetrated each layer to the layer beneath where applicable. After the third and final layer had been added and tamped, excess concrete was removed from the top of the cone and the base plate. Subsequently, the cone was lifted upwards within 5 seconds, in order to ensure that the true slump was obtained and that this was not influenced by the speed at which the cone was lifted. Afterwards, the cone was placed on the base plate and the difference in height between the top of the cone and top of the concrete measured. This measurement represents the slump of the concrete.
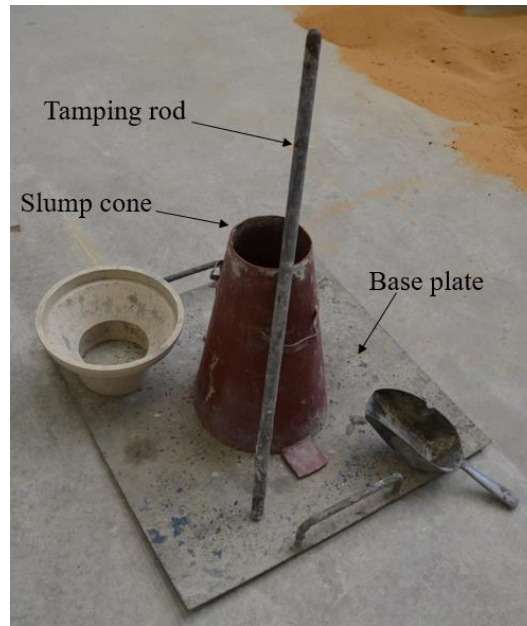
Figure 3.8: Equipment used to measure slump

3.5.2 Rheology

The rheological properties of the concrete mixes were assessed using the ICAR rheometer. This portable rheometer consists of a motor driving a four-bladed vane, which is inserted into a steel container containing the concrete. Table 3.7 shows the dimensions of the vane and the container, while Figure 3.9 depicts the rheometer.

Table 3.7: Specifications of ICAR rheometer

Vane radius (mm)	**63.5**
Vane height (mm)	127
Container radius (mm)	143
Height of filling of container (mm)	

With regards to the testing process of rheology, it was noted at what time water was added to the concrete during the mixing process described in Section 3.4.1.1. After the mixing process was finished, the rheometers bucket was filled with the particular concrete to a predetermined height and the top part of the rheometer, i.e. the motor and vane, was inserted into the concrete, as depicted in Figure 3.9 b). The testing process took place in a climate controlled room at a temperature of 25°C and relative humidity of 65%. Starting at 10 minutes after the addition of water to the mix, a stress growth test was conducted at a rotating speed of the vane of 0.025 revolutions per second (rev/s). After 15 seconds this test was stopped, the concrete was allowed to settle for 15 seconds, and test repeated at 0.05, 0.1, 0.25 and 0.5 rev/s, with the same procedure being followed for each test and

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between the tests. After the last test, the concrete was allowed to settle before a flow curve test with the specifications set out in Table 3.8 was conducted. This entailed the measurement of torque the vane experiences at certain pre-set rotating speeds. The Bingham model was then fitted to the data points by the software of the ICAR rheometer (Koehler & Fowler, 2004) to obtain the plastic viscosity and yield stress of the concrete. This procedure was repeated at times of 20, 30, 45 and 60 minutes after the addition of water to the mix.

The stress growth test was conducted as the static yield stress, discussed in Section 2.1.4.1, was deemed to be of interest. The flow curve test was conducted as this yields data points depicting the torque experienced at certain revolving speeds, which are used to calculate apparent values of the dynamic yield stress and viscosity of the concrete (Koehler & Fowler, 2004). These are valuable parameters as they accurately reflect rheological behaviour and allow for comparison between mixes.
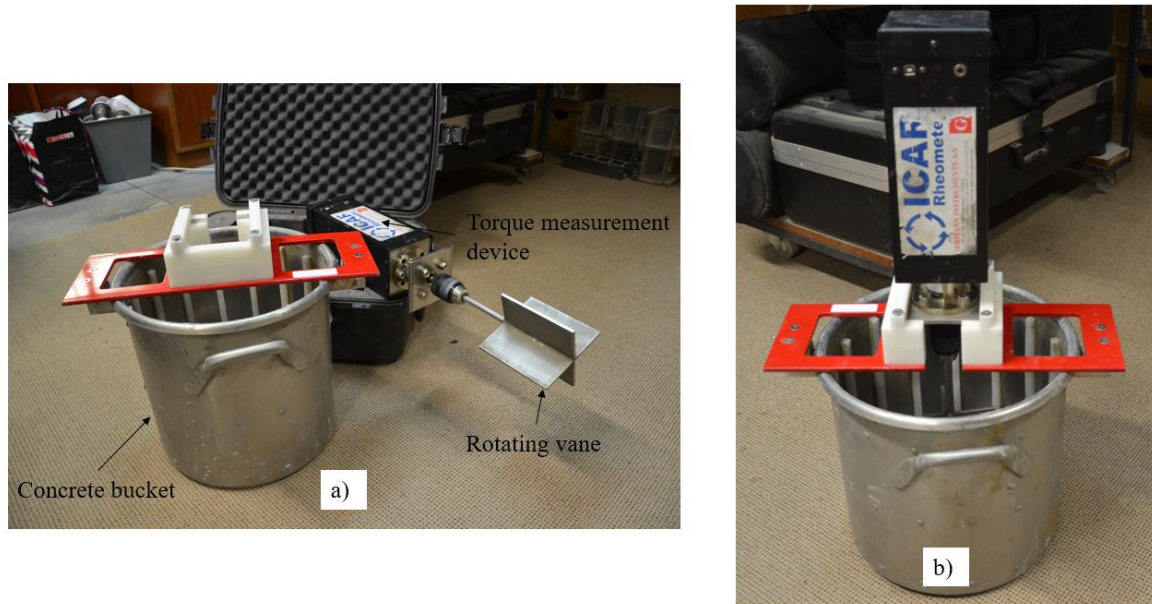
Figure 3.9: Picture of a) rheology measurement equipment and b) equipment held in place as during testing

Table 3.8: Test specifications for rheological flow curve

Breakdown time (s)	**20**
Breakdown speed (rev/s)	0.5
Initial speed (rev/s)	0.5
Final speed (rev/s)	0.05
Number of points	7
Time per point (s)	5

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3.5.3   Setting time

The setting time test was carried out according to SANS 50196-3 (SANS, 2006c). Although the method set out in this document is intended for cement paste, the test can also provide relevant information for mortar isolated from concrete mixes. Thus, the test was carried out as set out in the document, but on mortar separated from a concrete mix.

The prescribed Vicat apparatus, needles and setting time moulds were used in this test. These can be seen in Figure 3.10. To initiate the test, the time at which water was added to the dry concrete mix was noted, as this represents the start of the hydration reaction and setting process of concrete and is thus the zero time in the setting time test. After the mixing process was completed, as described in Section 3.4.1.1, the mortar was separated from the concrete mix by sieving the concrete through a sieve with an aperture size of 4.75 mm. A trowel was then used to fill the setting time moulds with the mortar, and it was ensured that the full volumes of these moulds were filled by applying downward pressure to the mortar with the trowel, before a surface finish was applied.
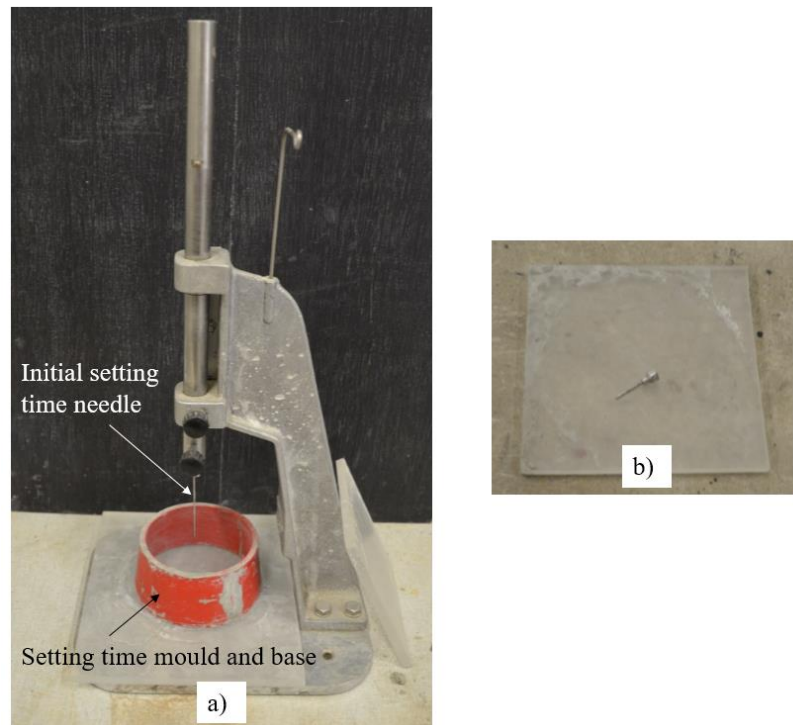
Figure 3.10: Setting time apparatus, with a) Vicat apparatus and b) final setting time needle

Subsequently, the testing of the samples commenced, taking place in a climate controlled room at a temperature of 25°C and relative humidity of 65%. During testing, the initial setting needle, attached to the Vicat apparatus, was dropped into the mortar specimen and the distance it penetrated was measured. The Vicat apparatus and all necessary equipment can be seen in Figure 3.10 a). Initial

setting time is defined as that time from time zero to the time when the needle penetrates to a depth of 6±3 mm from the base plate of the specimen. Once this is reached, the sample is inverted and measurements taken on the bottom surface, using the final setting needle seen in Figure 3.10 b). Eventually, the final setting time is that time from time zero to the time when the outer ring of the final setting needle does not make an imprint on the mortar surface. Readings were initially taken at intervals of 30 minutes. When setting of the concrete was noticed, these intervals were shortened to 10 minutes.

3.6   Tests of hardened properties

Tests took place on the concrete at various ages, in its hardened state. The tests were conducted according to the relevant standards and are described in the following sections.

3.6.1   Compressive strength

The compressive strength test was carried out according to SANS 5863 (SANS, 2006a). For this purpose, concrete cubes with dimensions 100 x 100 x 100 mm were cast as described in Section 3.4.2, of which three cubes were tested at each of the ages of 1, 3, 7, 28, 56 and 91 days. The test itself involved the cubes being taken from their respective curing tanks, and the exact dimensions of each cube being noted before testing. Subsequently, the cubes, still moist due to the curing process, were placed in a Contest compression testing machine, such that loading was applied perpendicularly to the casting direction. This machine can be seen in Figure 3.11 a). A steel plate was placed on top of the cube as seen in Figure 3.11 b), after which testing commenced.

Figure 3.11: Picture of a) contest machine and b) concrete cube and steel block in machine

A loading rate of 180 kN/min was applied to the cube by the machine, until failure was reached. The load that resulted in the failure was displayed by the machine and noted. The compressive strength of the concrete was then calculated by:

$$\sigma = \frac{F}{A}$$

(3.1)

with σ representing the compressive strength of the concrete (MPa), F representing the load that resulted in failure (N) and A representing the area of the surface to which the load was applied (mm^2).

3.6.2   Durability

In terms of the durability of the concrete the permeability of the concrete was found to be of value, as this is a major transport mechanism for materials causing deterioration of concrete. In this regard, the Oxygen Permeability Index (OPI) test was used to quantify permeability. It was carried out according to the Durability Index Testing Procedure Manual (Alexander, Ballim & Mackechnie, 1999).

Firstly, this involved the mixing, casting and curing of concrete as described in Sections 3.4.1, 3.4.2 and 3.4.3. At an age of 25 days, the concrete cubes were taken from the curing tanks and cores extracted using a hollow drillbit with an inner diameter of 70 mm. This took place by means of clamping the cube between two metal plates, and drilling through the cube, in a direction perpendicular to the original casting direction, using a high powered drill. This procedure was repeated for four cubes, in order to obtain four cores. Care was taken to not allow aggregate to spall from the sides of the cores.

Immediately after coring was completed, the outer 5 mm of concrete of each of the cores was cut off using a rotary saw. Following this, disks with a thickness of 25±2 mm were cut from each core using the same saw. It was again ascertained that no aggregate spalled from their surfaces. Once this process was complete, the specimen were placed in an oven for 7 days ± 4 hours, at a temperature of 50°C, after which the test commenced. Once the specimens were taken from the oven, they were allowed to cool down to the room temperature of the climate controlled room in which the tests were conducted, namely a temperature of 25°C and relative humidity of 65%. The diameters at two points, and thicknesses at four points of the samples were measured to the nearest 0.01 mm, using a digital calliper. Subsequently, testing commenced using the apparatus in Figure 3.12.

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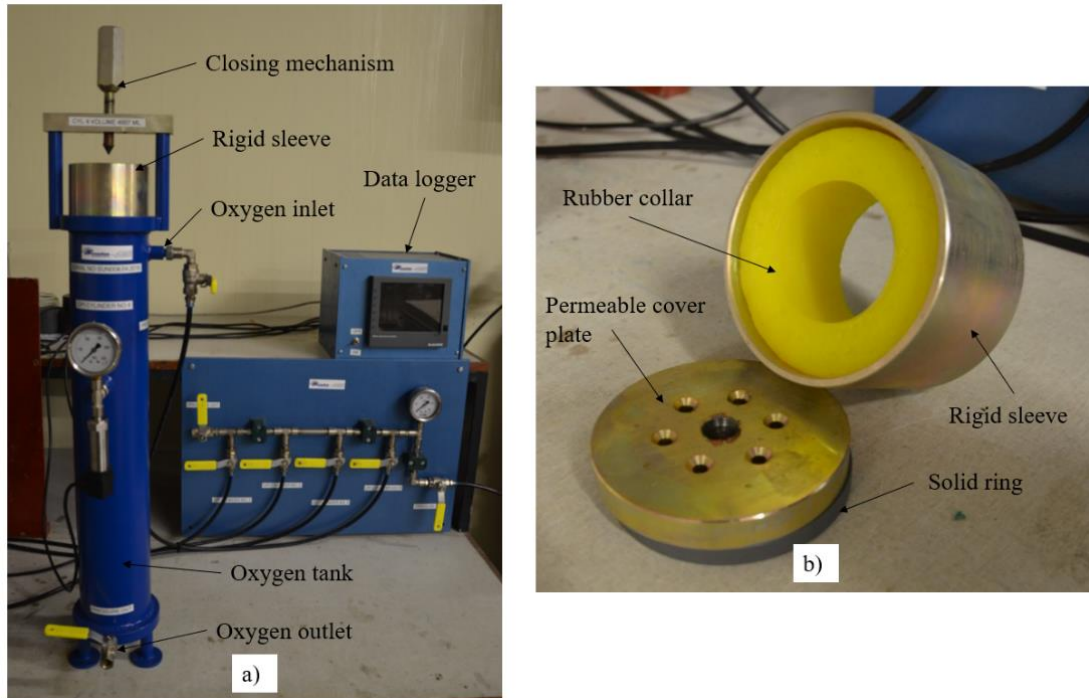
Figure 3.12: Picture of a) OPI apparatus and b) sleeve containing concrete specimen during test

The samples were inserted into rubber collars, so as to ensure a tight fit. These were subsequently inserted into rigid sleeves, again ensuring a tight fit. Following this, the sleeves were inserted into the OPI apparatus and the permeable cover plates seen in Figure 3.12b) inserted on top of the samples. The closing mechanisms were closed by tightening the screw and thus applying pressure to the cover plates, ensuring the horizontal expansion of the rubber collars beneath and thus preventing leakage. Screws were closed by hand, and further three half revolutions with a spanner. The four separate oxygen chambers were flooded with oxygen for five seconds with the outlet valves open, in order to remove any air. Afterwards, the outlet valves were closed and the pressure in the chambers allowed to build up to 100±5 kPa. Once this had been reached, all inlets were closed and the time noted simultaneously. Readings of the air pressure were taken regularly, in order to ensure that the pressure inside each chamber had not dropped by more than 5 kPa. The testing of a sample was completed after a time of 6 hours and 15 minutes, or if the air pressure inside the particular chamber dropped below 50 kPa.

In order to calculate the OPI value, linear regressions was used to plot a line of best fit, by plotting the natural logarithm of the original pressure over the pressure at a given time, against the time. The regression line was forced through the origin and the slope *z* determined by:

$$z = \frac{\sum \ln \left(\frac{P_0}{P_t}\right)^2}{\sum \ln \left(\frac{P_0}{P_t}\right) t} \tag{3.2}$$

with P_0 being the initial pressure at the start of the test (kPa), P_t being the pressure at a given time and t being the time since the start of the test (s). The value obtained by this equation was used to calculate the coefficient of permeability k using:

$$k = \frac{\omega V g d z}{R A \Theta} \tag{3.3}$$

with ω being the molecular mass of oxygen (32 g/mol), V being the volume of the particular oxygen chamber (l), g being the constant of gravitational aceleration (9.81 m/s^2), d being the average thickness of the specimen, z being the slope of the regression line determined previously, R being the universal gas constant (8.313 J/mol K), A being the cross sectional area of the specimen (m^2) and Θ being the absolute temperature (K). Finally, the OPI value was calculated using:

$$OPI = \log_{10} \frac{1}{n} \left(\sum_1^n k \right) \tag{3.4}$$

with k being the previously determined permeability coefficient while n is the number of these.

After the OPI had been established, the durability of the concrete could be defined to be "excellent", "good", "poor" or "very poor" according to guideline values obtained and given in Table 3.9 (Alexander & Magee, 1999).

Table 3.9: Values used to classify durability of concrete (Alexander & Magee, 1999)

	Excellent	**Good**	**Poor**	**Very poor**
OPI value	>10	9.5-10	9-9.5	<9

3.7   Tests of sustainability properties

Two methods were used to quantify the sustainability of the concrete mixes and present a comparison between the concrete mixes. These are described in the following sections.

3.7.1   Carbon emission study

In order to ultimately quantify the sustainability of a certain concrete mix, the equivalent carbon dioxide (CO_2) emissions due to the materials and their quantities in the mix are a useful indicator.

The term equivalent CO_2 emissions is a term used to describe a number of greenhouse gasses in a common unit, and this process is thus referred to as establishing the Greenhouse Warming Potential (GWP) of the mix. For this purpose, data was obtained, presenting the equivalent CO_2 emissions of all materials used per kilogram of that material (CO_{2e}/kg). With the exception of ground limestone, all data was obtained for South African conditions and thus deemed to be applicable. Due to lack of South African data for ground limestone, European data was used in this regard. The data can be seen in Table 3.10 (Cement and Concrete Institute, 2010; Proske *et al.*, 2014). The GWP for each mix was established per cubic meter of that mix, and thus the quantity of a particular material in a mix (kg) was simply multiplied by its particular GWP value (kg CO_{2e}/kg) as seen in Table 3.10. Finally, the contributions of all materials in a mix were summed to establish the total GWP of that mix.

Table 3.10: Data used in carbon emission study (Cement and Concrete Institute, 2010; Proske et al., 2014)

Material	GWP (kg CO_{2e}/kg)
CEM I cement	0.818
Fly ash	0.002
Ground limestone	0.028
Sand	0.005
Stone	0.005
Superplasticiser	0.220
Accelerator	0.220

3.7.2   Cement and carbon dioxide intensity index study

Equations 2.23 and 2.24 were modified and used to determine the cement and carbon dioxide intensity indices, ci and CO_{2e}-i respectively. Equation 2.23 was modified by replacing the binder content used to calculate the binder intensity (bi) index with the cement content of the particular mix to calculate the ci index. This was done as cement is responsible for the majority of CO_2 emissions due to concrete, and it was thus assumed to be most valuable to determine its efficient use, rather than including all binders in the calculation, as these have a small influence on the total GWP. The cement content (kg/m^3) and GWP (kg CO_{2e}/m^3) of the particular mix for which these indices were determined was thus substituted into Equation 2.23 and 2.24 respectively, and compressive strength at 28, 56 and 91 days taken as the unit of functional performance. These ages were chosen as 28 day strength is the most widely used design parameter for concrete. Furthermore, the 56 and 91 day strength was of interest because of the possibility to optimise mixes according to project specific requirements, i.e. concrete not having to reach strength at 28 days. The indices thus enabled an assessment of the mixes efficiency and sustainability over time, and comparisons thereof.

3.8   Concluding summary

This chapter provided the experimental framework according to which the investigation was conducted. Firstly, the methodologies of the entire study, as well as all the procedures which formed part of the study are provided. Following this, the materials used are elaborated on, and some of their respective properties highlighted. Subsequently, pre-experimental procedures are laid out, as well as the procedure of the tests on the concrete during the course of this investigation. The next chapter provides results and a discussion of the replacement of cement by SCM and fillers.

Chapter 4

Cement Replacement by Supplementary Cementitious Materials and Fillers

This chapter presents the results of the development of a concrete with high cement replacement levels by supplementary cementitious materials (SCM) and fillers, namely fly ash and ground limestone. Firstly, the mix designs that were developed, all meeting the previously mentioned initial workability requirements, are shown and discussed. This is followed by the results of tests on plastic and hardened properties of these concrete mixes, and the discussion of these results. Subsequently, the sustainability properties of these mixes are discussed. Finally, a concluding summary is provided, once again mentioning the most important aspects of this range of concrete mixes.

4.1   Concrete mix designs

The mix designs that were devised with the replacement of cement by fly ash, and fly ash and ground limestone can be seen in Table 4.1 and 4.2 respectively. These were created by aiming for the previously mentioned target slump of 100 mm and adjusting the water content as needed.

Table 4.1: Mix designs of reference mix, mixes with SCM

Mix	REF	FA20	FA40	FA60	FA80
Water (kg/m³)	215	200	188	175	170
Cement (kg/m³)	430	320	226	140	68
Fly ash (kg/m³)	0	80	150	210	272
Fine sand (kg/m³)	358	378	393	411	413
Coarse sand (kg/m³)	358	378	393	411	413
Stone (kg/m³)	1050	1050	1050	1050	1050

Table 4.2: Mix designs of mixes with SCM and filler

Mix	FA10GL10	FA20GL10	FA20GL20	FA30GL20	FA30GL30
Water (kg/m³)	192	190	190	185	180
Cement (kg/m³)	307	266	228	185	144
Fly ash (kg/m³)	38	76	76	111	108
Limestone (kg/m³)	38	38	76	74	108
Fine sand (kg/m³)	399	397	395	400	409
Coarse sand (kg/m³)	399	397	395	400	409
Stone (kg/m³)	1050	1050	1050	1050	1050

The naming of mixes is described in Section 3.4.4. The Mix REF refers to the reference mix, with no cement replacement. The mix designs give a first impression of the achievable reduction in binder content, and cement content specifically. It can be seen that an increased replacement of cement by

fly ash, and the combination of fly ash and ground limestone resulted in an increasingly lower water requirement at constant slump. Accordingly, this firstly implies a generally lower total binder content the higher the cement replacement levels, and secondly, the higher replacement levels specifically imply a lower cement content. The cement content is thus reduced dramatically. It can be seen that the use of only fly ash, and the combination of fly ash and ground limestone have similar effects on the reduction of water requirement and binder content: the mixes FA20 and FA10GL10, FA40 and FA20GL20, and FA60 and FA30GL30 all have a similar water requirement and cement content. Fly ash and ground limestone can thus both be deemed to be beneficial towards the retention of workability of concrete at lower water contents.

4.2   Plastic properties of concrete

This section focusses on the results obtained for the tests conducted on the concrete mixes in their plastic state. Firstly, information regarding the consistency of the mixes are given. Following this, the results of the rheological tests are provided. Finally, the results of the setting time tests on the mixes can be seen.

4.2.1   Consistency

Consistency as a property of concrete refers to its slump, segregation and general uniformity. While the slump of all mixes was confirmed to be 100 ± 10 mm by means of the slump test, the segregation and general uniformity were assessed visually. All mixes were confirmed to have no segregation and be generally uniform, before they could be used in further tests.

4.2.2   Rheology

With regard to the rheology, the flow curve test at 10 minutes was found to be the most valuable, as it gives the best indication of the dynamic yield stress and plastic viscosity of the concrete in its fresh state. The stress growth test results were distorted by the vane getting stuck on aggregate at certain time intervals, thus causing the torque and static yield stress measurement to be abnormally high. These results were therefore not used. Furthermore, the dynamic yield stress has in the past been preferred over the static yield stress, as it is associated with the "full structural breakdown and the beginning of plastic flow" (Liddel & Boger, 1996; Saak, Jennings & Shah, 2001; Koehler & Fowler, 2004). The results of the flow curve test, in terms of the plastic viscosity and dynamic yield stress of the mixes, can be seen in Figure 4.1. The values of plastic viscosity and dynamic yield stress, the R^2 values of the fit of the flow curves and the flow curves for all mixes can be seen in Appendix B. Challenges regarding the compatibility of the rheometer and certain concrete mixes were also experienced for the flow curve test, resulting in insufficient R^2 values of the Bingham model for certain tests, as the data points do not fit the Bingham model. This could possibly be attributed to the

rotating vane getting stuck on some of the large aggregate which accumulated during testing, which resulted in higher than usual measurements of torque and an inaccurate representation of the rheology when the Bingham model was fitted to these data points. Data with R^2 values lower than 0.7 was deemed to be unsatisfactory. In Figure 4.1, mixes for which unsatisfactory R^2 values were obtained are indicated by cross-shaped markers, while those with satisfactory values are indicated by circular markers. The former mixes offer limited statistical relevance to make accurate conclusions.
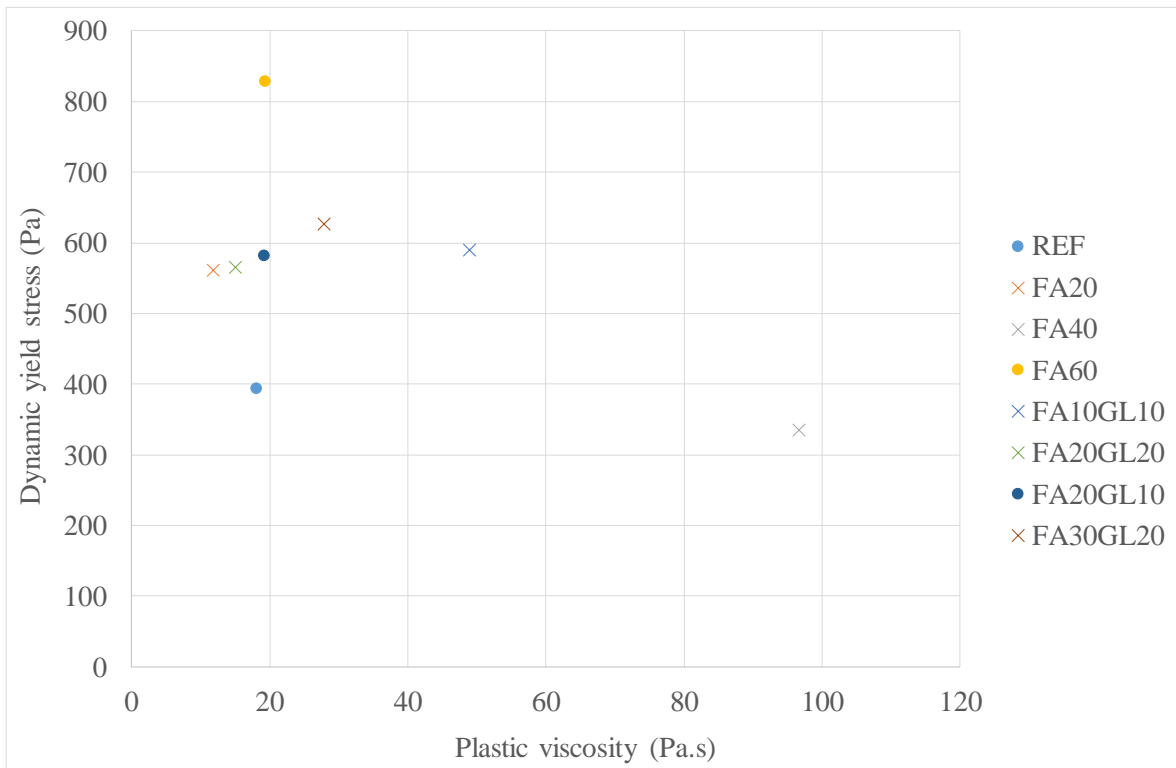
Figure 4.1: Yield stress and plastic viscosity of mixes with SCM and filler

Firstly, it is observed that the R^2 values of the majority of mixes in this section are inadequate and thus need to be interpreted carefully. However, for those mixes with adequate R^2 values, a clear trend can be identified. Although they have similar values of plastic viscosity, mixes with a greater cement replacement level are shown to have a higher yield stress. These results have potential implications on the replacement of cement by, for instance, fly ash in concrete for use in practice. In this regard, fly ash has been widely used and added to reduce the yield stress of concrete, as it is known to reduce the yield stress at replacement levels between 10% and 20% of cement and thus improve consistence (Szecsy, 1997; Tattersall, 2014). Furthermore, fly ash has been added to concrete mixes as it has been assumed to increase viscosity, and thus prevent segregation. However, throughout the mix development process in practice a constant slump in accordance with a reference mix is aimed for.

These results show that at a constant slump, cement replacement by fly ash and limestone has an effect contrary to that intended when used in practice: it increases yield stresses while causing the concrete to maintain constant viscosity. Although the mixes with inadequate R^2 values offer unreliable data, a similar trend can be observed for them. Mixes with greater levels of cement replacement exhibit greater yield stresses while a relatively constant viscosity is maintained, except for Mixes FA40 and FA10GL10 which, predictably, have the lowest values of R^2 of all mixes.

4.2.3 Setting time

The results of the setting time test for the mixes can be seen in Figure 4.2. It must be noted that the setting times of all mixes were normalised according to Mix REF, which has an initial setting time of 330 min and final setting time of 410 min. Furthermore, Mix FA80 was omitted from this test as it became apparent during initial mixing and casting that its setting times were delayed significantly and thus inadequate.

From the results it can be seen that the replacement of cement by fly ash, and fly ash and ground limestone delays the setting of the concrete, in terms of both the initial and final setting time. The results show that the greater the fraction of cement replaced, the greater the delay in setting. This behaviour was expected when fly ash was used, as it has previously been shown that this material delays the setting of concrete, and the more of it is present, the more this effect becomes evident. However, contrary to what was predicted, the limestone did not accelerate the setting of the concrete (Bonavetti *et al.*, 2003). The reasons for this could be fourfold: firstly, the fly ash in the mixes incorporating limestone could have negated the effect that limestone has on the setting time. Furthermore, the amounts of limestone in those mixes could have been too little to have a measurable influence on the setting time, as it has previously been shown that influences become apparent above replacement levels of 20% of pure limestone (Bonavetti *et al.*, 2003). Thirdly, it has been shown that finer limestone has a greater effect on setting time. Although the limestone used in this investigation is relatively fine, the choice of a finer limestone could perhaps be motivated in this regard. However, the most likely reason for this behaviour is the use of limestone as a cement replacement instead of as a filler, replacing sand. The reduced cement content due to this possibly results in a less pronounced hydration reaction, thus delaying setting. Furthermore, the limestone is effective in creating an alkaline environment, which further aids the hydration reaction (Bonavetti *et al.*, 2003).

Nonetheless, the delayed setting times pose a practical challenge, especially at replacement levels of 40% and above. The delayed final setting time to 725 min and more for the FA40 and FA60 mixes impedes the practical applicability. Thus, the use of an accelerator as a way to counter this was investigated. The results of this can be seen in Figure 4.3.

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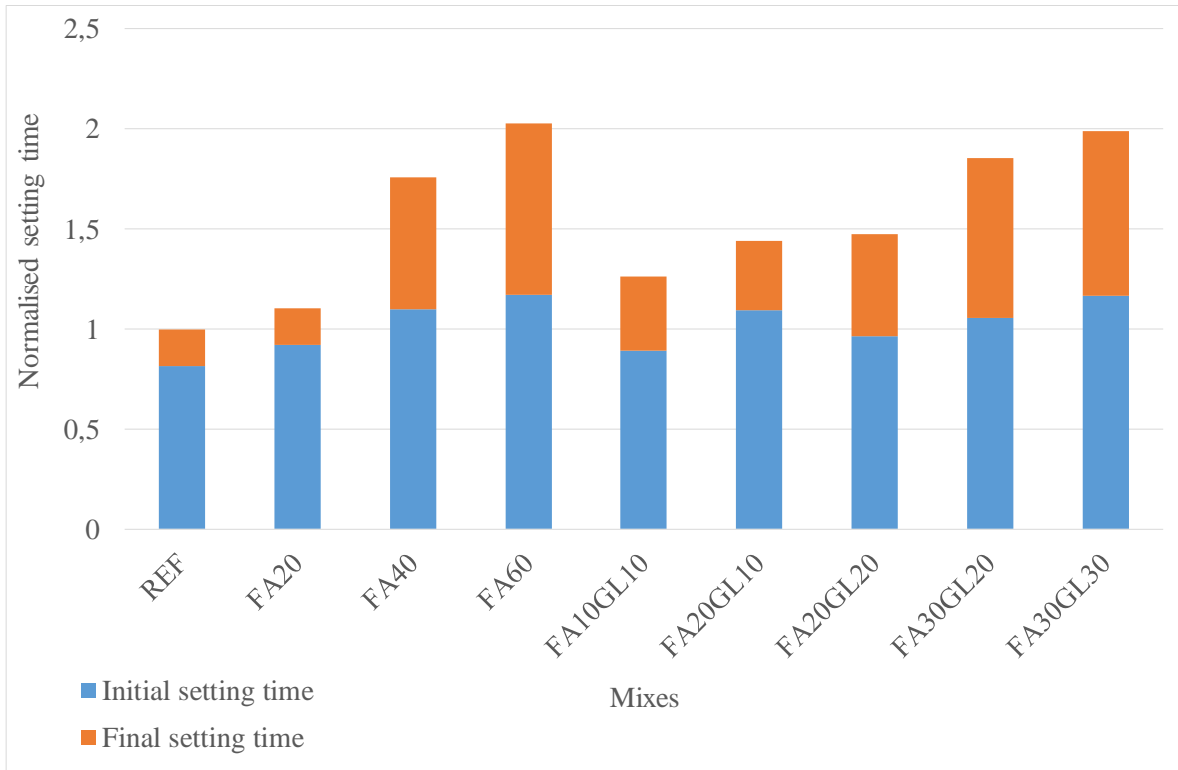
Figure 4.2: Normalised setting times of reference mix, mixes with SCM and filler
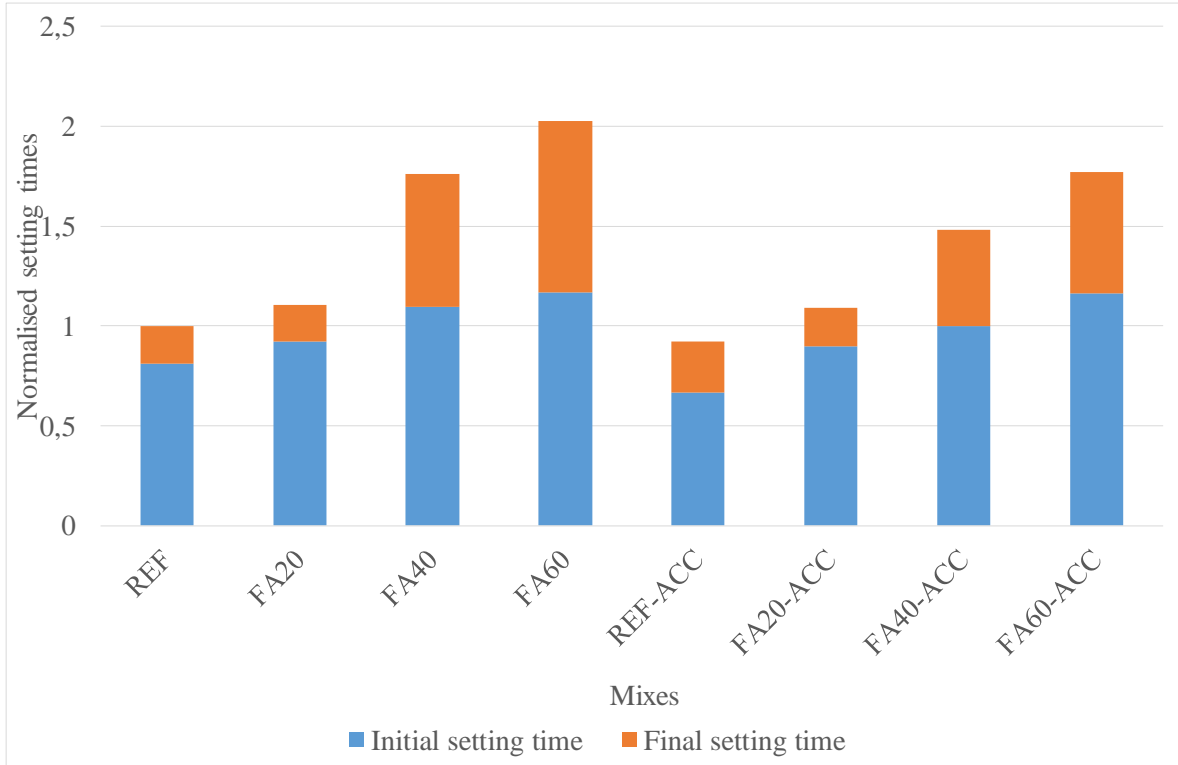
Figure 4.3: Normalised setting times of mixes containing accelerator

The results show that after the inclusion of an accelerator, the setting times were significantly reduced for all mixes, by an average of 10%. Therefore, the use of an accelerator is a possibility should the delayed setting time prove to be a serious challenge to the practical applicability of the concrete mixes.

4.3   Hardened properties of concrete

This section provides the results of the tests on the concrete mixes in their hardened state. Firstly, the results of the compressive strength tests are provided. Subsequently, the results of the OPI test, used to assess the durability of the concrete mixes, are given.

4.3.1   Compressive strength

The results of the compressive strength tests of these mixes can be seen in Figure 4.4. Mix FA30GL30 was omitted after 28 days, due to inadequate compressive strength when compared to the reference mix and FA60, with the same cement replacement level. Mix FA80 was omitted completely as it reached no significant strength at 7 days.
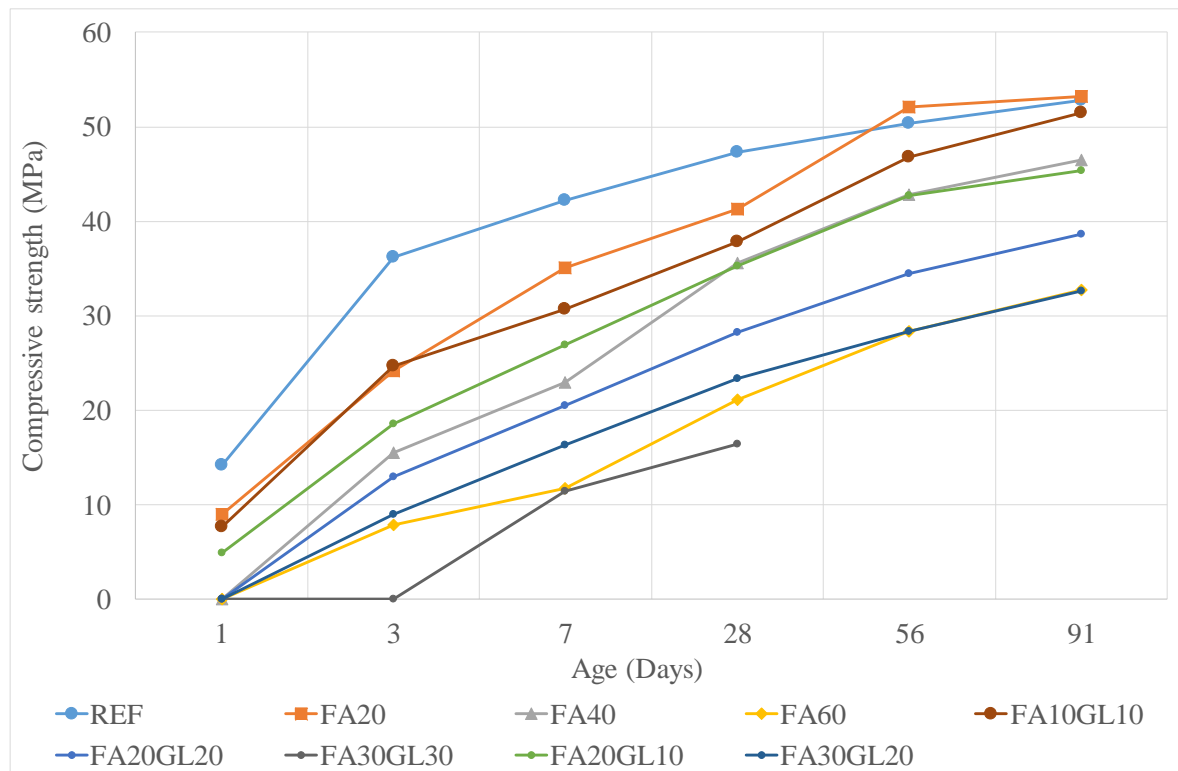
Figure 4.4: Compressive strength of mixes with SCM and filler

The results agree with the known conventional strength gain patterns of concrete. The reference mix REF reached a compressive strength of 47 MPa at 28 days, allowing its classification as a medium

to high strength concrete with approximately double the sufficient strength for conventional practical application (Roberts & Marshall, 2010).

With regard to the early age strength of the concrete, Mix REF shows the highest rate of strength gain initially. The greater the cement replacement level, by fly ash and limestone, the lower the rate of strength gain. This can be attributed to the known delayed strength gain of fly ash and the chemical inertness of limestone. The positive influence limestone supposedly has on the early age strength of concrete up to one day age is not evident, possibly due to the large organic content of the limestone again influencing its behaviour. Up to a 28 day age the results show that the higher the cement replacement level, the lower the strength. Mixes with only fly ash replacing the cement perform slightly better than comparable mixes with fly ash and limestone, for instance when comparing Mixes FA20 and FA10GL10. This indicates the pozzolanic behaviour of fly ash compared to the inertness of limestone.

At ages greater than 28 days the results illustrate the renowned strength gain of fly ash at later ages. All mixes with fly ash, as well as fly ash and limestone show higher rates of strength gain than Mix REF between ages 28 and 91 days. Mix FA20 surpasses the strength of Mix REF at ages 56 and 91 days. At age 91 days, mixes with fly ash again reach higher strengths than those with fly ash and limestone. This becomes particularly obvious at higher cement replacement levels, i.e. higher amounts of fly ash and limestone. Mix FA60, with the highest cement replacement level, reaches a strength of around 33 MPa at 91 days, giving it sufficient compressive strength for application in many practical instances at this age.

4.3.2   Durability

The values obtained during the OPI test can be seen in Table 4.3. According to the guideline values in Table 3.9, all mixes except for Mix FA30GL20 have good or excellent OPI values, therefore being sufficiently impermeable and durable.

Table 4.3: OPI values of mixes with SCM and filler

Mix	REF	FA20	FA40	FA10GL10	FA20GL10	FA20GL20	FA30GL20
OPI value	9.68	9.94	10.13	10.01	9.96	9.8	9.36

Furthermore, the results show that the more cement is replaced by fly ash, the higher the OPI value. This confirms that greater amounts of fly ash result in decreased permeability and improve the durability of concrete. Contrary to this, the limestone adversely impacted the permeability and durability. In this regard, the larger the fraction of cement replaced by fly ash and limestone, the

lower the OPI value was, and thus the higher the permeability. This could be attributed to less hydration reaction products being formed due to the replacement of cement by inert limestone, again motivating its use as a filler rather than a cement replacement.

4.4   Sustainability study

The results of the study on the sustainability is presented in this section. Firstly, the sustainability of the mixes in terms of the equivalent CO_2 emissions (CO_{2e}) of the mixes is discussed. Following this, the binder and carbon dioxide intensity indices of the mixes are presented.

4.4.1   Carbon emission study

The carbon emission study entailed calculating the Greenhouse Warming Potential (GWP) of the mixes. These are presented in Figure 4.5, normalised according to Mix REF, which has a GWP of 361 kg CO_{2e}/m^3 concrete. As can be seen, cement is the material that contributes the majority of CO_{2e} emissions for all mixes, which again highlights the need for its replacement or reduction in concrete.
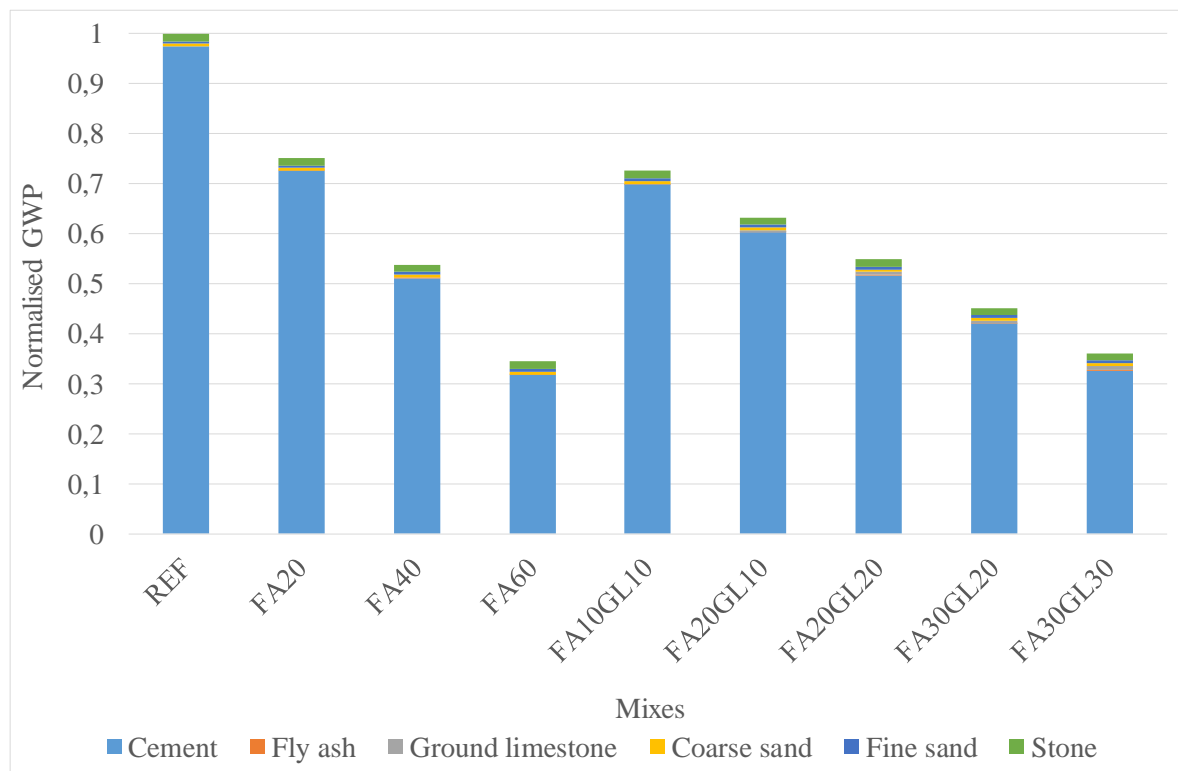
Figure 4.5: Normalised GWP of reference mix, mixes with SCM and filler

The results show that the substitution of cement by fly ash and ground limestone has a significant impact in terms of reducing the GWP of the mixes. Firstly, this is due to the more favourable CO_{2e} emissions during the production of these materials, when compared to those of cement. Secondly, it is due to the materials' water reducing capabilities in the mixes, and the subsequent lower total binder

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content in the mixes. This also explains the trend of a greater reduction in GWP at greater replacement levels of cement.

When comparing mixes with the same cement replacement fractions, with either fly ash or fly ash and limestone replacing cement (e.g. FA20 and FA10GL10), it can be seen that the two materials have similar capabilities in reducing the GWP, with fly ash having slightly superior qualities. They are thus both valuable materials to use in this regard.

4.4.2   Cement and carbon dioxide intensity index

The cement intensity (ci) and carbon dioxide intensity (CO_{2e}-i) indices can be seen in Figure 4.6 and 4.7. Mix FA30GL30 was not tested for compressive strength at ages 56 and 91 days, thus not making it possible to determine the indices with these functional performance parameters.
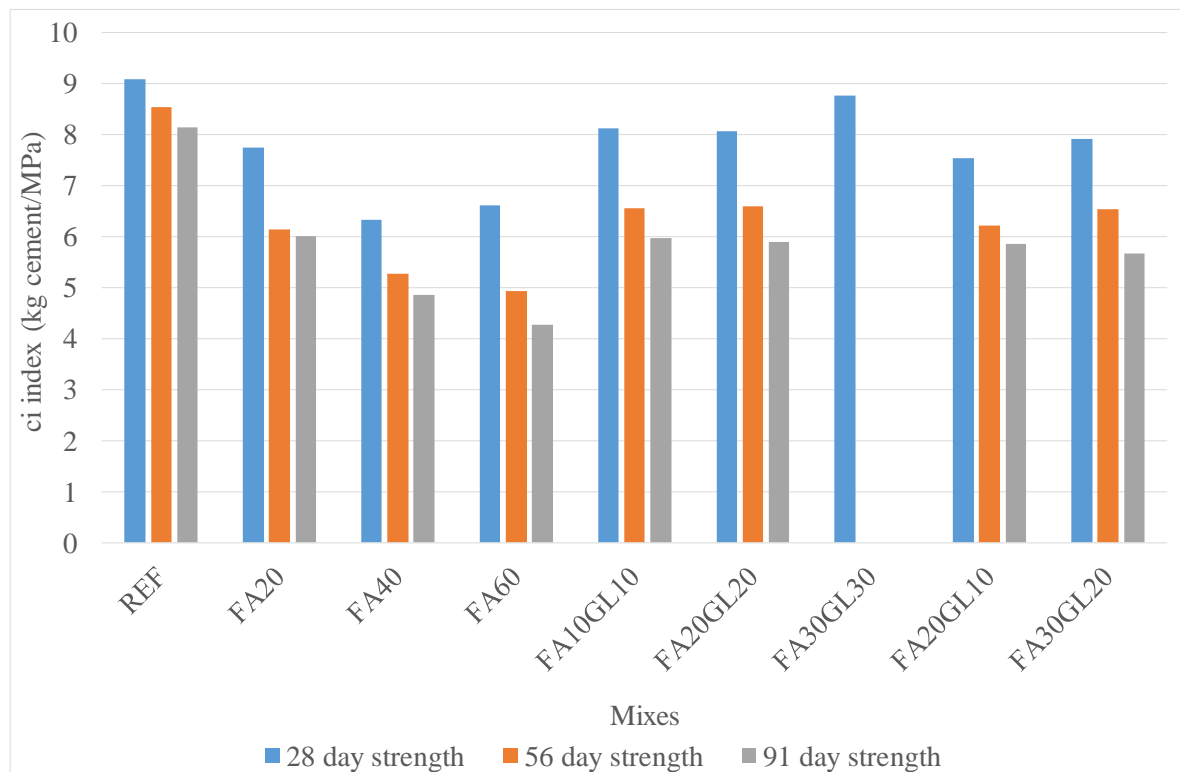
Figure 4.6: Ci indices of mixes containing SCM and filler

It can be seen that all mixes with cement replacement have lower ci indices than Mix REF at all ages. This indicates that less cement is used to produce 1 MPa of strength for the former mixes, making them more efficient, and ultimately more sustainable, than Mix REF. This increase in efficiency is not only due to the reduction in cement content, but also due to the preservation of compressive strength up to certain replacement levels. This also explains the decrease in efficiency in mixes with higher cement replacement levels at certain ages, and mixes with fly ash *and* limestone as a

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replacement. It was previously shown that these mixes have substantially lower compressive strengths than Mix REF. Due to the definition of the ci index, this causes the indices of these mixes to increase, even though the mixes themselves have lower cement contents than Mix REF. They thus "lose" efficiency in this sense. However, this also implies that the indices have to be compared at various ages, as they are thus also influenced by the later strength gain of fly ash. For instance Mix FA40 shows the optimal combination of reduced cement content and compressive strength at age 28 days, due to its good compressive strength. However, at ages 56 and 91 days Mix FA60 has a lower ci index than Mix FA40. This highlights the need for the design of concrete according to specific requirements in practice. If, for instance, strength is only required at ages 56 and 91 days, certain mixes might prove to more efficient than alternatives which function well at age 28 days.

It has previously been shown that for 20 MPa strength concrete at 28 days the minimum binder index (bi) is 13 kg binder/MPa, while for a 60 MPa this value is 5 kg binder/MPa (Damineli *et al.*, 2010). The obtained values of the mixes, which have a strength range of 16 MPa to 47 MPa at 28 days for Mixes FA30GL30 and REF respectively, fall well within this range and thus provide a good reference.
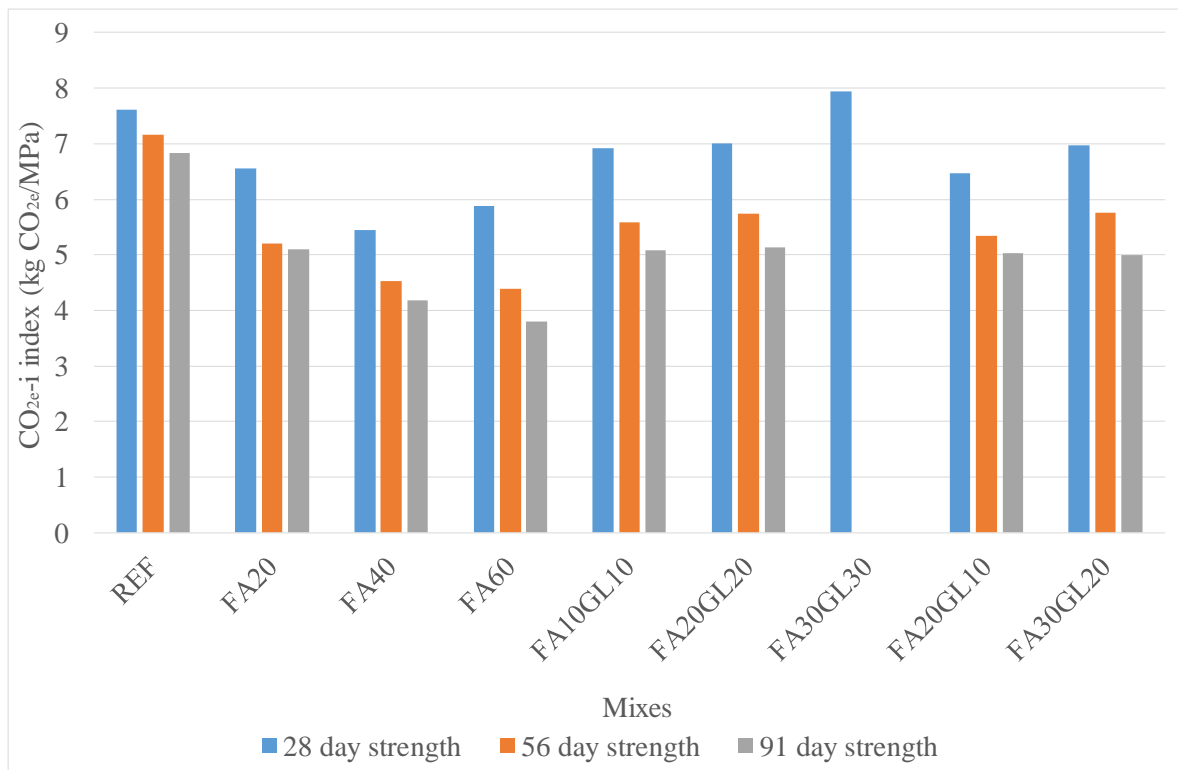
Figure 4.7: CO_{2e}-i indices of mixes containing SCM and filler

Due to the large share that cement has in the GWP of each mix, and the relatively low contribution of fly ash and limestone to this, the CO_{2e}-i indices of the mixes follow the same trend as the ci indices. Again, it can be seen that greater replacement levels result in more efficiency, for mixes with fly ash as a replacement. This is similarly due to their relative upkeep of compressive strength. Furthermore their increased efficiency at later ages should be highlighted, which points out the need for design of concrete according to specific, project-dependent requirements, as a measure of maximising efficiency and ultimately sustainability of the concrete.

4.5   Concluding summary

This chapter described the development of a reference mix with standard constituents, as well the development of mixes in which fractions of the cement in this reference mix were replaced at constant slump and water/binder ratio. The fly ash and limestone both showed water reducing capabilities, thus permitting lower water and binder contents the higher the fraction of cement replaced.

When considering rheology, the most important finding was that an increased replacement of cement by fly ash or fly ash and limestone at constant slump resulted in an increased dynamic yield stress at relatively constant viscosity. This is relevant as these cement replacement materials are used to reduce the water requirement of the concrete and could thus be assumed to reduce the yield stress. This was found not to be the case when a constant slump is maintained. Mixes with a replacement level of 60% were found to have double the yield stress of the Mix REF, thus limiting the replacement fraction that would result in tolerable rheological properties to 40% of cement, i.e. Mix FA40.

With regard to setting time, a greater replacement fraction of cement was found to have a delayed setting time, especially in mixes in which only fly ash was used to replace cement. Limestone was not found to have the expected accelerating effect on setting time.

A higher cement replacement fraction was found to result in lower compressive strength, at ages up to 28 days. Mixes which contained fly ash as a cement replacement were found to have more strength than similar mixes in which cement was replaced by fly ash and limestone. After 28 days, the fly ash in the mixes caused significant strength increases. Mixes up to a replacement level of 40% (i.e. FA40) showed sufficient compressive strength, especially at ages up to 91 days. This highlights the need for the development of mixes for project specific requirements.

The OPI tests that were conducted to quantify the permeability, and ultimately durability of the mixes showed that all mixes, except FA30GL20, have good or excellent durability. An increasing cement replacement by fly ash resulted in improved durability. The higher the fraction of cement replaced

by fly ash and limestone, the worse the durability. Thus, mixes FA20, FA40, FA10GL10, FA20GL10 and FA20GL20 qualify for further use in this regard.

The GWP of each mix was established as part of the sustainability study. Due to the large extent that cement contributes towards this it was found that the larger the fraction of cement replaced, the lower the GWP of the mix and therefore the more sustainable it is. The smallest fraction replaced, i.e. 20% of cement, already showed a 25% decrease in GWP, thus emphasising the sustainability potential of all mixes.

Finally the ci and CO_{2e}-i indices of the mixes were established and found to follow the same trend, again due to the large contribution cement has toward the equivalent CO_2 emissions of the mix. All mixes showed significant improvements in the indices, especially at later ages, and thus all present viable solutions. Mixes FA40 and FA60 performed best in this regard, due to the combination of their low cement content and the relatively high compressive strength at 91 days due to the fly ash.

From these results it can be concluded that cement replacement levels up to 40% (i.e. Mix FA40) displayed adequate properties in all tests conducted. Emphasis was thus placed on these mixes when using the further approaches to create the optimised mixes. However, the inclusion of superplasticiser could further improve the properties of these mixes, as well as those with cement replacements up to 60%. The results achieved by the inclusion of superplasticiser in these mixes are presented and discussed in Chapter 5.

Chapter 5

Cement Content Reduction by Superplasticisers

This chapter focusses on the reduction of water requirement of concrete by the use of high range water reducing admixtures, and the subsequent binder-content reduction at a constant water/binder ratio. More specifically, the water requirement, and subsequently binder-content, of the mixes previously established in Chapter 4 was reduced by means of these admixtures, and new mixes were devised. Firstly, the mix designs of these newly established concrete mixes are presented and discussed, all meeting the previously mentioned initial workability requirements. Thereafter, the results of tests on the plastic and hardened properties of these concrete mixes are presented and discussed separately. Following this, the sustainability properties of the concrete mixes are shown and discussed. Lastly, a concluding summary, discussing the most important aspects of these mixes, is provided.

5.1   Concrete mix designs

The mix designs of the mixes in which both PCE and acrylic polymer based superplasticisers were included are shown in Table 5.1 and 5.2, as well as the reference mix design in order to enable comparison between the mixes. As discussed in Sections 3.1.2 and 3.3.4, the superplasticisers were added to the previously determined mixes at dosages determined using the Marsh cone test, aiming for a constant slump by reducing the water content of the previously determined mixes. The Mix FA80 was eliminated by this stage, due to unsatisfactory compressive strength.

The naming of the mixes is clarified in Section 3.4.4. Comparing the reference mixes with and without superplasticisers, it can be seen that the inclusion of both superplasticisers resulted in substantial reductions of water requirement, and thus binder content. With the exception of the Mix REF-MAP, it was again observed that higher replacement levels of cement result in lower water requirement at a constant slump, and thus a lower total binder content. No explanation can be found for the significantly lower water requirement of mix REF-MAP.

When one compares the PCE based and acrylic polymer based superplasticisers in equivalent mixes, it can be seen that the PCE based superplasticiser is slightly more effective in reducing the water requirement, and ultimately binder content of concrete. However, their capabilities in this regard are similar and both types of superplasticiser can generally be deemed effective.

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Table 5.1: Mix designs of reference mix, mixes with PCE superplasticiser

Mix	REF	REF-PCE	FA20-PCE	FA40-PCE	FA60-PCE
Water (kg/m³)	215	173	160	150	138
Cement (kg/m³)	430	346	256	180	110
Fly ash (kg/m³)	0	0	64	120	166
Fine sand (kg/m³)	358	448	466	479	498
Coarse sand (kg/m³)	358	448	466	479	498
Stone (kg/m³)	1050	1050	1050	1050	1050
Superplasticiser (kg/m³)	-	3.11	2.24	1.8	2.21

Table 5.2: Mix designs of mixes with MAP superplasticiser

Mix	REF	REF-MAP	FA20-MAP	FA40-MAP	FA60-MAP
Water (kg/m³)	215	152	162	155	149
Cement (kg/m³)	430	304	259	186	119
Fly ash (kg/m³)	0	0	64	124	179
Fine sand (kg/m³)	358	493	461	467	472
Coarse sand (kg/m³)	358	493	461	467	472
Stone (kg/m³)	1050	1050	1050	1050	1050
Superplasticiser (kg/m³)	-	3.04	1.94	1.55	1.79

As discussed in Section 3.1.2, the optimal dosage of each cement/binder combination established using the Marsh cone test was doubled, and new mixes developed with this doubled dosage. However this was only conducted using the PCE based superplasticiser, as the doubling of the superplasticiser dosage for the MAP based superplasticiser would have caused the dosage to be above the recommended dosage of the supplier. The newly developed mixes again had the constant target slump of 100±10 mm and can be seen in Table 5.3.

Table 5.3: Mixes with double the optimal dosage

Mix	REF-1.8PCE	FA20-1.4PCE	FA40-1.2PCE	FA60-1.6PCE
Water (kg/m³)	163	152	145	130
Cement (kg/m³)	326	243	174	104
Fly ash (kg/m³)	0	61	116	156
Fine sand (kg/m³)	469	484	490	516
Coarse sand (kg/m³)	469	484	490	516
Stone (kg/m³)	1050	1050	1050	1050
Superplasticiser (kg/m³)	5.87	4.26	3.48	4.16

When comparing these mixes to the corresponding original mixes with the optimal dosage of superplasticiser determined by the Marsh cone test, it can be seen that the water requirement of the mixes is not reduced drastically between the two sets of mixes. This gives a first indication of the

validity of the Marsh cone test, namely that in terms of reducing the water requirement of concrete at a constant slump, it presents a dosage that is close to the optimal dosage.

5.2 Plastic properties of concrete

The results of the tests on the previously established concrete mixes in their plastic state can be seen in this section. Firstly, information regarding the mixes consistency, and associated properties, is provided. Subsequently, results of the rheology tests are shown. Finally, results of the setting time tests are given and discussed.

5.2.1 Consistency

As part of the assessment of consistency, the slump, segregation and general uniformity of the concrete mixes were assessed. While the former was assessed by means of the slump test and confirmed to be 100±10 mm for each mix, the latter were assessed visually. In order for the mixes to qualify for further use, no segregation should have been observed and the mix should have been uniform. This was confirmed to be the case for all previously mentioned mixes.

Difficulty was experienced in establishing the mixes with double the dosage established by the Marsh cone and still meeting the target slump. Their slumps were found to be very sensitive to the smallest changes in water content and the mixes were found to be particularly sticky, and could thus be impractical when used in practice.

5.2.2 Rheology

The results of the rheological tests on the mixes containing both superplasticisers at the optimal dosage, as well as the PCE superplasticiser at double dosage and Mix REF, can be seen in Figure 5.1. Again the results of the flow curve test 10 minutes after mixing were used, as they give a good indication of the concrete in its fresh state, and due to challenges occurring during the stress growth test. For two mixes, inadequate R^2 values lower than 0.7 were obtained for the data and the Bingham model fitted to it. This could again be attributed to the rotating vane getting stuck on some of the large aggregate, which tended to accumulate during testing. The unsatisfactory data is indicated by cross shaped markers in Figure 5.1, while satisfactory data is indicated by circular markers.

The first observation that can be made is that the majority of R^2 values are adequate and the data can be considered reliable. With regard to this data, it can be seen that both superplasticisers generally cause an increase in plastic viscosity at specific cement replacement levels, when comparing the mixes to Mix REF. Specifically the PCE based superplasticiser has a significant effect on the plastic viscosity, which becomes more prominent when its dosage is doubled, causing the viscosity to increase substantially. This effect is more pronounced at cement replacement levels up to 20%, as

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higher replacement levels result in similar plastic viscosities to Mix REF. Mixes REF-MAP and FA20-MAP do not depict this trend, possibly due to their statistical flaws. Although the effect of increased plastic viscosity in concrete mixes can be practically useful due to a correspondingly lower chance of segregation, excessive viscosity is considered undesirable. The previously mentioned stickiness of the mixes with double the Marsh cone dosage is an example of an undesired effect due to excessive viscosity, as it made the concrete unworkable, and not pumpable and prone to air entrainment in practice. The dosage established by the Marsh cone could thus prove to be more suitable than the double dosage with regard to plastic viscosity.
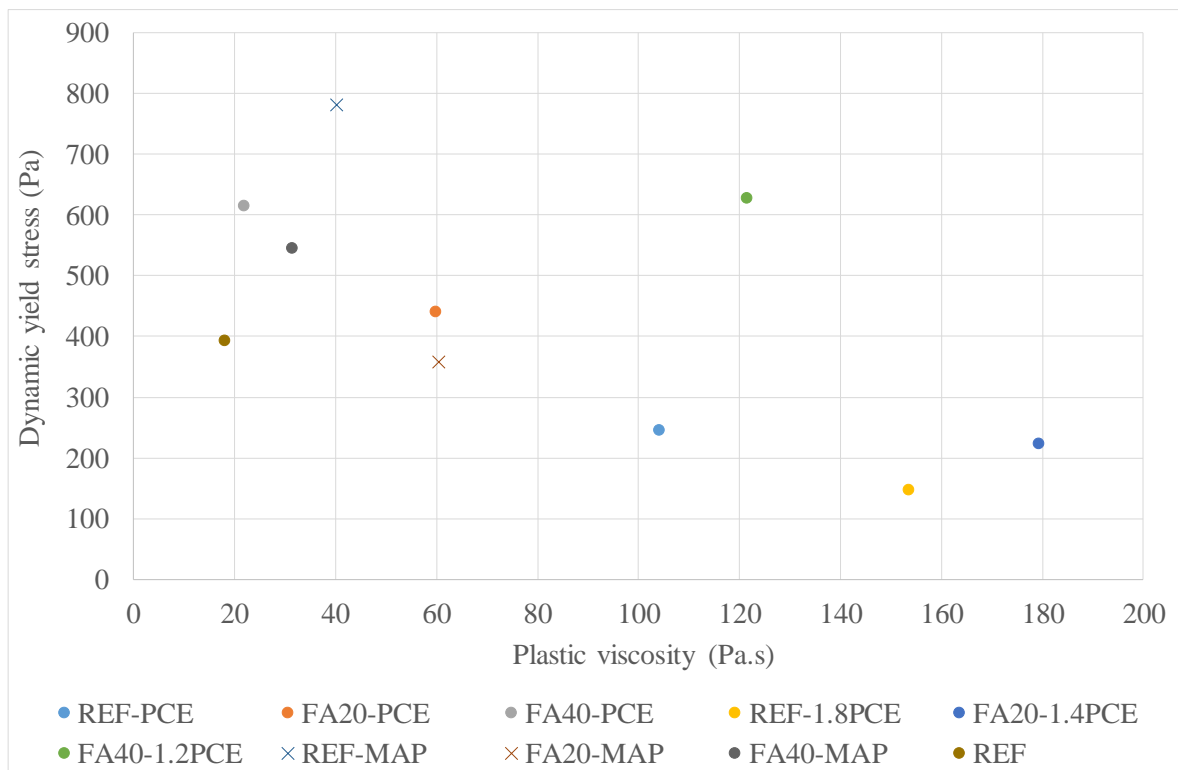
Figure 5.1: Yield stress and plastic viscosity of mixes with optimal and double dosage superplasticisers

When comparing these mixes to Mix REF in terms of yield stress, it is observed that the inclusion of superplasticisers resulted in a decrease or similar yield stresses for lower cement replacement levels up to 20%. As observed during the replacement of cement by fly ash previously, at higher replacement levels the yield stress increased compared to REF. However, the inclusion of a superplasticiser reduces the severity of this effect, as can be seen when comparing mixes with comparable replacement levels in Figure 4.1 and 5.1. Again, mixes REF-MAP and FA20-MAP do not show this trend, which can be attributed to their insufficient R^2 values. It can thus be concluded that the use of superplasticiser is particularly beneficial at low levels of cement replacement, as it

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produces a concrete with slightly higher, but not excessive, viscosity, and thus lowers the chance of segregation. It also lowers the yield stress, resulting in a better consistency of the concrete and making it more workable and practically usable. Although Mixes REF-MAP and FA20-MAP proved to be statistically irrelevant, Mix FA40-MAP exhibited more favourable rheological properties than the comparable mix FA40-PCE, i.e. a slightly higher viscosity and lower yield stress. This could motivate a preference of the former over the latter.

5.2.3   Setting times

The results of the setting time tests can be seen in Figure 5.2 and 5.3. The results were normalised according to the initial and final setting times of the reference mix REF, which is included in Figure 5.2 to enable a visual comparison. The initial and final setting times of Mix REF are 330 min and 410 min respectively.
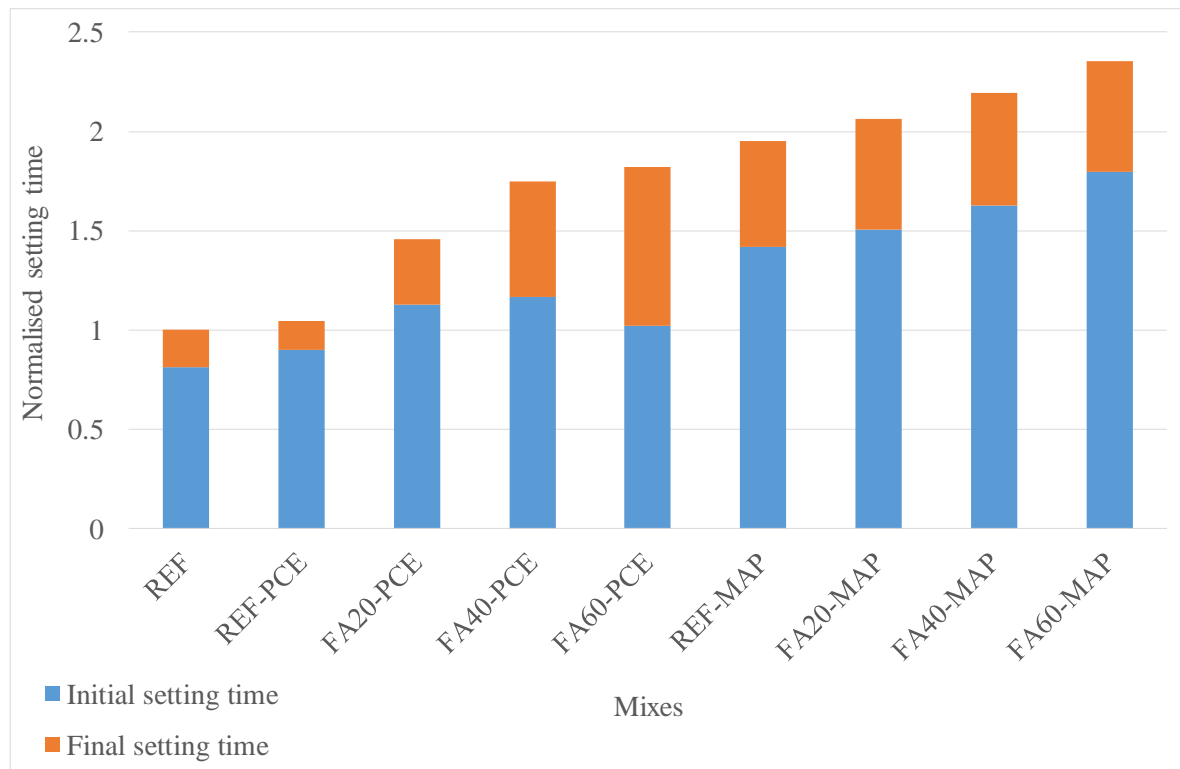
Figure 5.2: Normalised setting times of reference mix and mixes with superplasticisers

As can be seen in Figure 5.2, the inclusion of a superplasticiser influences the setting time to a varying degree, depending on the type of superplasticiser. The setting times of corresponding mixes with and without a PCE superplasticiser are very similar, as can be seen from Mixes REF and REF-PCE and other corresponding mixes in Figure 5.2 and Figure 4.2. Therefore, this type of superplasticiser does not seem to have a retarding effect on the hydration reaction at the dosage determined using the Marsh

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cone. However, the same can not be said for the acrylic based superplasticiser. When comparing the mixes using this superplasticiser to the corresponding mixes without superplasticiser and the PCE based superplasticiser, it becomes apparent that it, firstly, delays the setting of the concrete greatly and, secondly, does so to a far greater extent than the PCE based superplasticiser. This behaviour has previously been observed (Zhang & Kong, 2014).

When comparing the corresponding mixes in Figure 5.2 and 5.3, it can be observed that the doubling of the optimal dosage has a pronounced effect on the setting time, increasing it drastically. This suggests that the extent to which superplasticisers delay the setting of concrete is dependent on dosage.
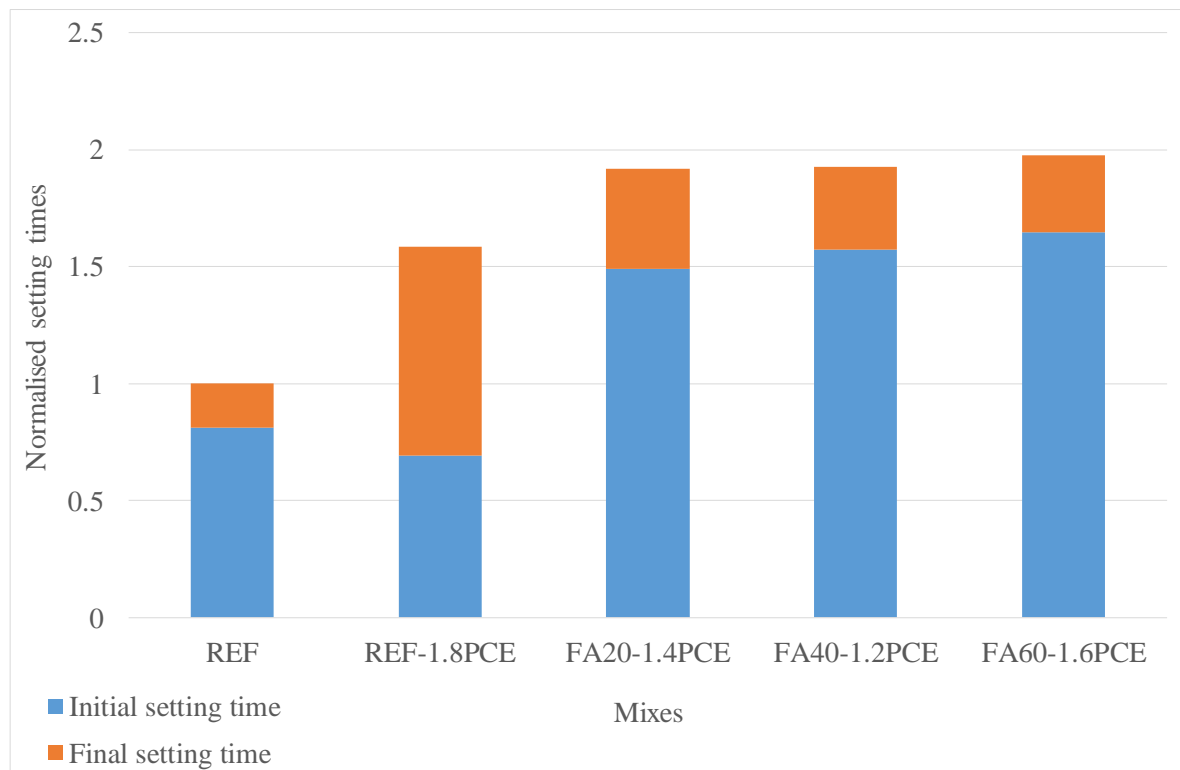
Figure 5.3: Normalised setting times of mixes with double optimal dosage

5.3   Hardened properties of concrete

This section provides results of the tests on the concrete mixes in their hardened state. Firstly, results of the compressive strength tests are provided. Following this, the results of the durability assessment of the concrete mixes are given.

5.3.1   Compressive strength

The results of the compressive strength tests can be seen in Figure 5.4 and 5.5. Figure 5.4 presents the compressive strengths of the mixes with optimal dosages of PCE and acrylic based superplasticisers, while Figure 5.5 presents those of the mixes with double the optimal dosage. No strength data is available for Mixes FA60-MAP and FA60-1.6PCE after an age of 28 days.
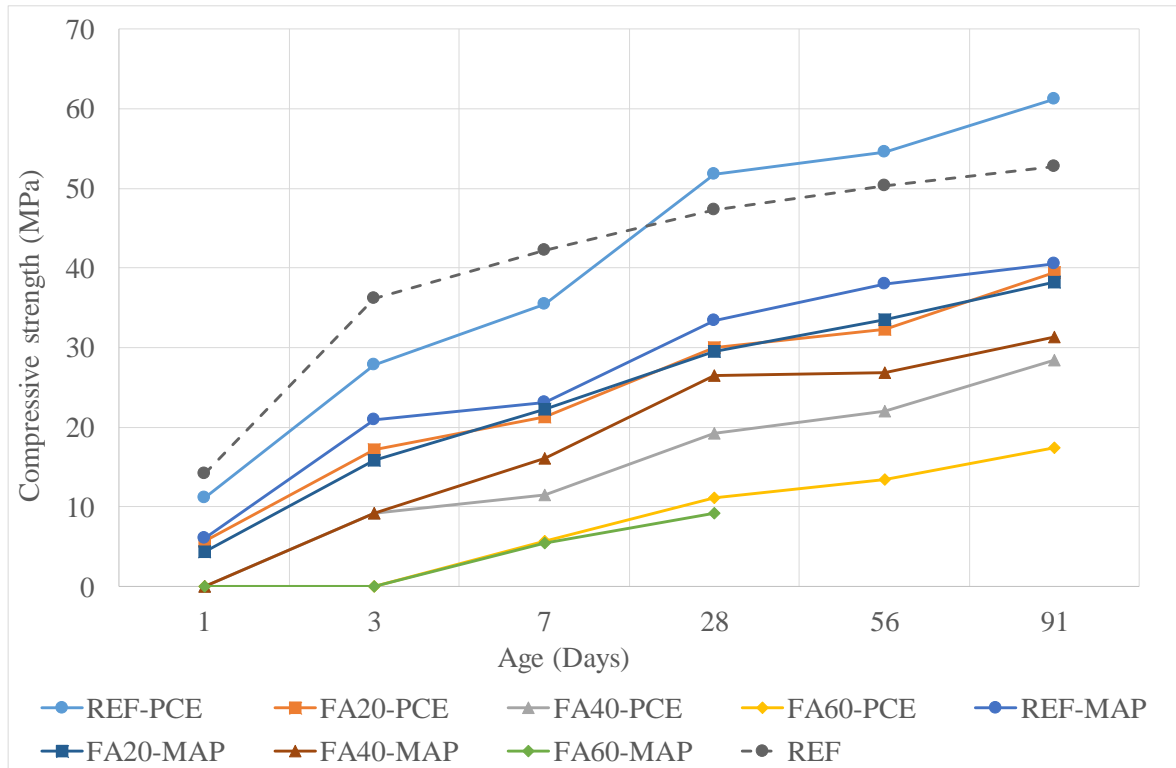
Figure 5.4: Compressive strength of mixes with superplasticisers

All mixes exhibit the strength development behaviour generally observed in concrete. At early ages up to 7 days, the strength development of the mixes with superplasticiser is slower than that of the reference Mix REF. This is partly due to the replacement of cement by fly ash in some of these, having the mentioned effect of delaying the strength gain of concrete the more cement is replaced. However, it is also due to the inclusion of superplasticiser. It could be argued that this delays the hydration reaction of cement, as already seen by its effect on the setting time of concrete. This, combined with the lower total cement content when superplasticiser is included at a constant slump, results in a lower strength gain rate. With the exception of Mix REF-MAP, the two types of superplasticiser have similar effects on the compressive strength up to 28 days. The low compressive strength of REF-MAP at 28 days and before when compared to REF and REF-PCE could be attributed to its questionably low cement content.

At later ages from 28 to 91 days, the development of strength of the mixes containing fly ash is similar to less pronounced than seen in Chapter 4. While mix REF-PCE shows substantial strength gains and strength at 91 days when compared to Mixes REF and REF-MAP, Mix MAP performs equally well or better at cement replacement levels of 20 and 40%.

When comparing the mixes with equivalent replacement fractions with double the optimal dosage to those with the optimal dosage, as well as the equivalent mixes in Figure 4.4, it can be seen that doubling the dosage has a positive impact on the compressive strength. For the mix with double the dosage, with no cement replacement and at replacement levels of 20% and 40%, significantly higher strength at 28 days is reached compared to those using the optimal dosage, suggesting better strength development at early ages. Furthermore, the mixes develop substantial strength after 28 days, until 91 days. This causes FA20-1.4PCE to surpass the strength of reference mix REF and its reference Mix FA20.
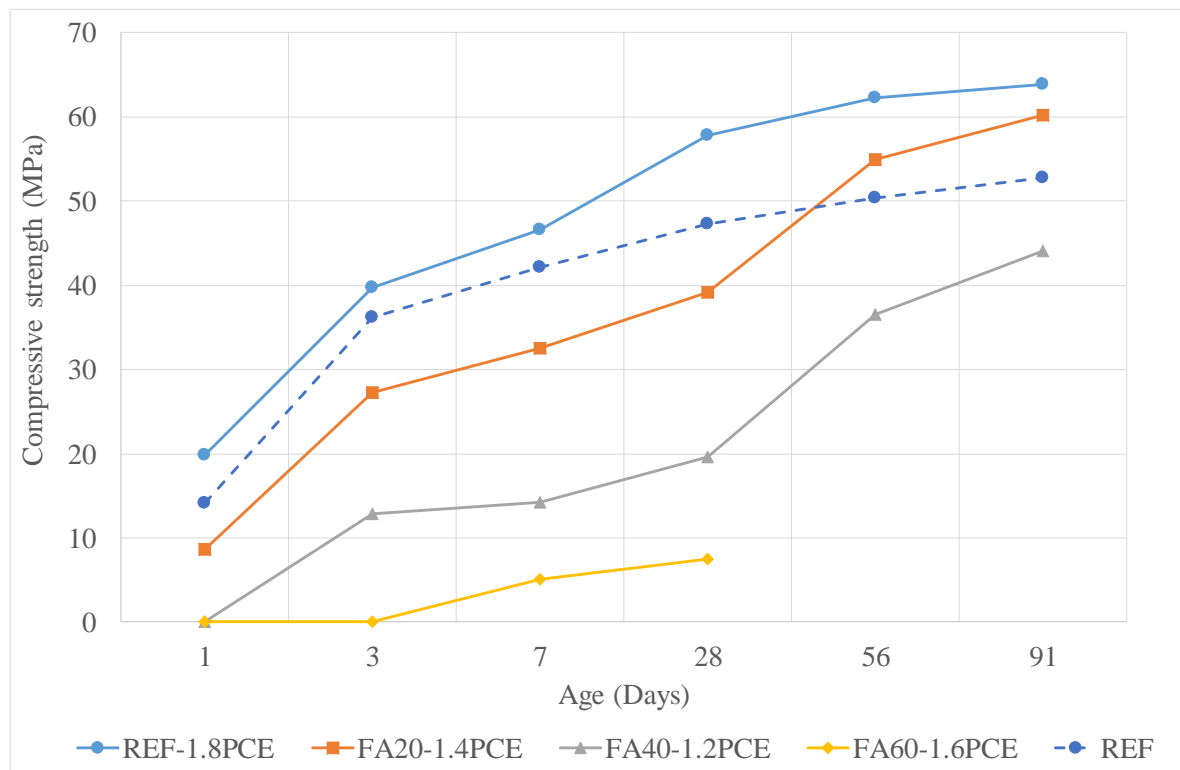
Figure 5.5: Compressive strength of mixes with double optimal dosage

These results again suggest a working relationship limited to the cement and superplasticiser. The lower strengths reached at lower cement contents and the lower dosage suggests that perhaps there is not enough superplasticiser available to activate the cement to gain compressive strength, which becomes especially prominent at low cement contents. The fact that strength increases when the

dosage is doubled shows that the superplasticiser seems to target, and activate, the cement. Furthermore, it seems to target the cement and work with the cement more so than with fly ash. This could confirm the findings of the initial Marsh cone test, as described in Section 3.3.3, which found a similar relationship between and limited to the cement and superplasticiser.

5.3.2   Durability

The OPI values of the reference mix and mixes with PCE superplasticiser, mixes with acrylic based superplasticiser and the mixes with double the optimal dosage can be seen in Tables 5.4 to 5.6 respectively. The results show that the OPI values of all mixes could either be classified as "good" or "excellent" according to Table 3.9.

Table 5.4: OPI values of reference mix, mixes with PCE superplasticiser

Mix	REF	REF-PCE	FA20-PCE	FA40-PCE
OPI value	9.68	10.45	10.34	10.01

Table 5.5: OPI values of mixes with acrylic based superplasticiser

Mix	REF-MAP	FA20-MAP	FA40-MAP
OPI value	9.75	10.27	10.21

When comparing the OPI values of the mixes in Table 5.4 and Table 5.5 to each other, and the corresponding mixes without superplasticiser in Table 4.3, it can be seen that the mixes with superplasticiser have higher OPI values and are thus less permeable and more durable. This could be explained by the better dispersion of cement particles due to the plasticising mechanism of the superplasticisers. This causes hydration products to form more uniformly and more distributed, thus leaving less room for voids and causing permeability to decrease. The two superplasticisers seem to have similar capabilities in ensuring durability. With the exception of Mix REF-MAP, the equivalent mixes have similar OPI values, with the acrylic superplasticiser perhaps working slightly better at higher cement replacement levels.

However, a different trend to the one observed in Chapter 4 is seen when superplasticisers are included. With the exception of Mix REF-MAP, a higher replacement fraction of fly ash in the mixes with superplasticiser is seen to result in lower OPI values, contrary to the trend observed in the mixes without superplasticisers. This could possibly be explained by the interaction between the superplasticisers and the cement and fly ash. Although the superplasticisers distribute these particles more uniformly, thus reducing permeability, it could become less effective when cement is replaced by fly ash above a certain limit, thus causing permeability to be higher at lower cement replacement

fractions. This again suggests a particular interaction between the superplasticiser and cement. Namely that the superplasticisers targets and activates the cement more so than the fly ash, thus causing more hydration products to form and impermeability to be higher when cement contents are higher.

Table 5.6: OPI values of mixes with double optimal dosage

Mix	REF-1.8PCE	FA20-1.4PCE	FA40-1.2PCE
OPI value	10.34	10.37	10.3

When comparing the OPI values of the mixes in Table 5.4 and 5.6, no clear trend can be identified. However, it can be seen that the doubling of the dosage does not seem to have a significant effect on the OPI values, as they generally are in the same range. Although this might seem insignificant, the similar permeability of the corresponding mixes could be interpreted as cement particles in the corresponding mixes being dispersed to the same extent. This would imply that the PCE superplasticiser is similarly effective in dispersing cement particles at the dosage determined by the Marsh cone and double the dosage, thus suggesting that the former, lower dosage is indeed the optimal dosage. This would validate the Marsh cone test as an effective test of the dispersal mechanism of superplasticisers. Furthermore, the similar OPI values of Mixes FA20-1.4PCE and FA40-1.2PCE to Mix REF-1.8PCE suggest that the lower cement contents in the former mixes have formed a similar amount of hydration products as the latter mix. This differs from the results of the tests where the single Marsh cone dosage was used, which showed the OPI values to decrease at higher cement replacement. It could thus again point to an interaction between the superplasticiser and cement, as more superplasticiser results in similar OPI values of the mixes in Table 5.6, as well as higher OPI values for comparable mixes in Tables 5.6 and 5.4 (i.e. FA40-PCE and FA40-1.4PCE).

5.4   Sustainability study

This section presents the studies carried out in order to determine the sustainability of the mixes. Firstly, the equivalent CO_2 emissions due to each mix are presented. Subsequently, the binder and carbon dioxide intensity indices are presented.

5.4.1   Carbon emission study

The Greenhouse Warming Potential was calculated during the carbon emission study, and the results of this are shown in Figure 5.6. These were normalised according to Mix REF, which has a GWP of 361 kg CO_{2e}/m^3 concrete. As can be seen, the greater part of the contributions towards the GWP of all mixes was due to cement, while superplasticisers have negligible contributions.
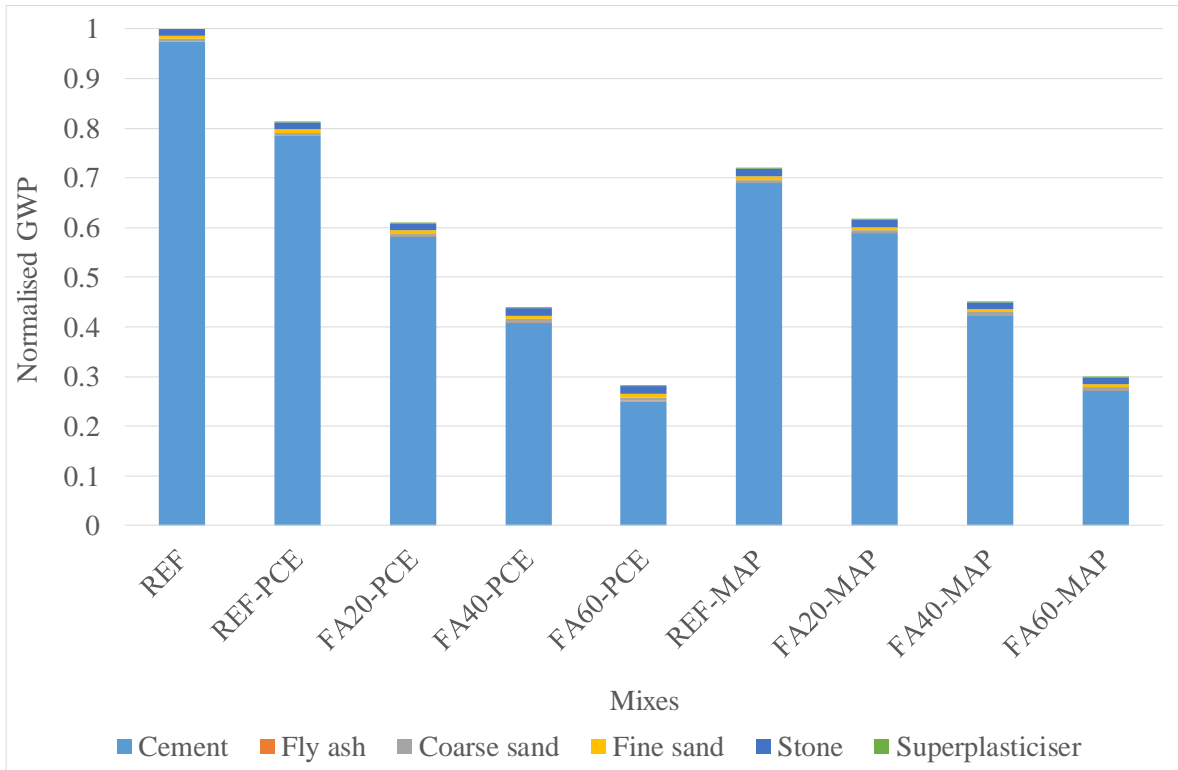
Figure 5.6: Normalised GWP of mixes with superplasticiser
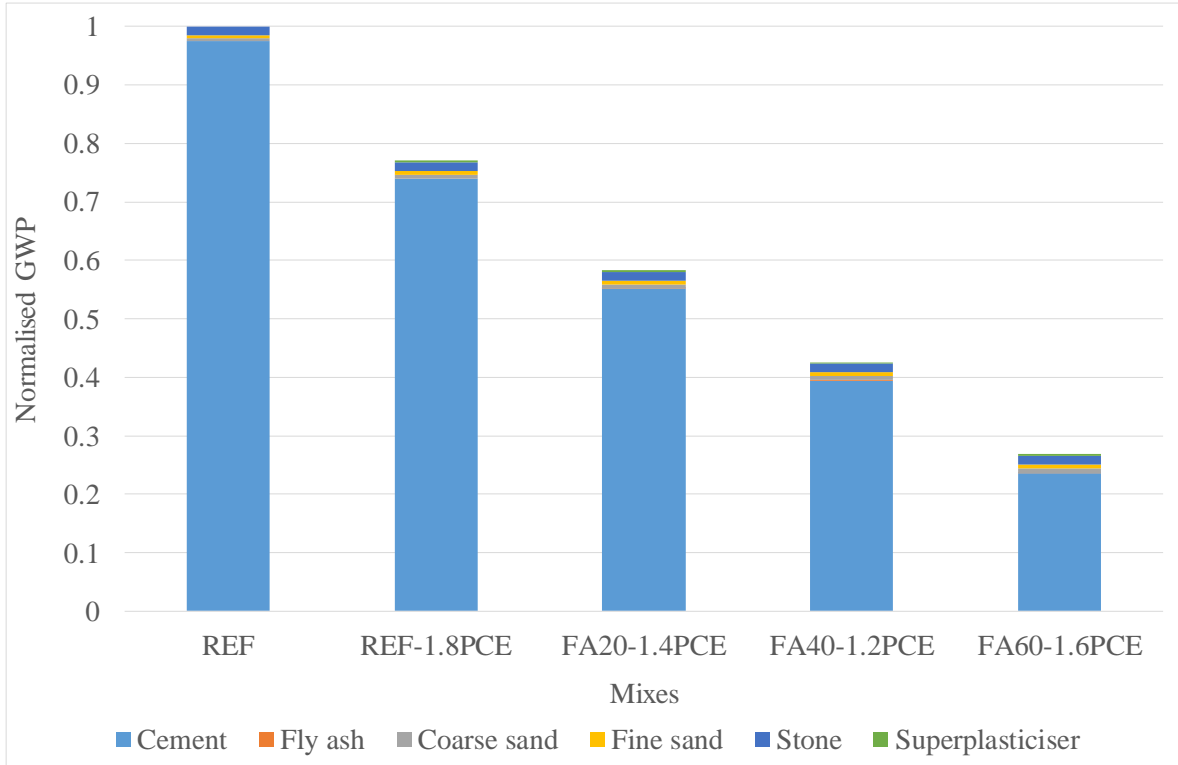
Figure 5.7: GWP of mixes with double optimal dosage

The results show that the replacement of cement results in decreases of the GWP. Furthermore, the addition of superplasticisers to these mixes results in further decreases of the GWP, which is observed when comparing the mixes to the reference mix REF and equivalent mixes in Figure 4.3. For instance, the addition of a superplasticiser results in a 20-30% reduction compared to Mix REF. A reduction in GWP of about 20% can be observed for all cement replacement levels. Although Mix REF-MAP shows a greater reduction in the GWP than mix REF-PCE, other equivalent mixes show a similar capability of both superplasticisers in reducing the GWP, and none of the two can be considered superior in this regard.

The GWP associated with the mixes with double the optimal dosage of superplasticiser can be seen in Figure 5.7. When comparing these to the equivalent mixes containing the optimal dosage, a reduction in GWP of at most 5% can be seen. The effect of the double dosage in this regard can thus be considered negligible when compared to the significant reductions between the reference mixes and the mixes containing the optimal dosage.

5.4.2   Cement and carbon dioxide intensity index

The cement intensity (ci) and carbon dioxide intensity (CO_{2e}-i) indices of the mixes with the optimal dosage of superplasticiser can be seen in Figures 5.8 and 5.9, while those of the mixes with double the optimal dosage can be seen in Figures 5.10 and 5.11. As no compressive strength data is available for Mixes FA60-MAP and FA60-1.6PCE after 28 days, the indices can not be determined at these ages. Generally, it can be seen that the indices again follow the same trend, due to the large contribution of cement to the GWP and the almost negligible contributions of the other materials. The two indices can therefore be discussed interchangeably in this regard.

When analysing the results, it is seen that when 28 day strength is used as functional performance indicator, only two mixes provide a prominent reduction in the ci and CO_{2e}-i indices, these being REF-PCE and FA40-MAP. This is attributed to the relatively low compressive strength of the mixes, as their cement content and GWP have shown substantial reductions. However, noticeable reductions in the indices occur at ages of 56 and especially 91 days. At the latter age, most mixes have substantially better indices than Mix REF, due to their additional strength development at later ages when compared to this mix. This highlights the need for project specific requirements in terms of target compressive strength at certain ages, in order to ensure maximum efficiency.
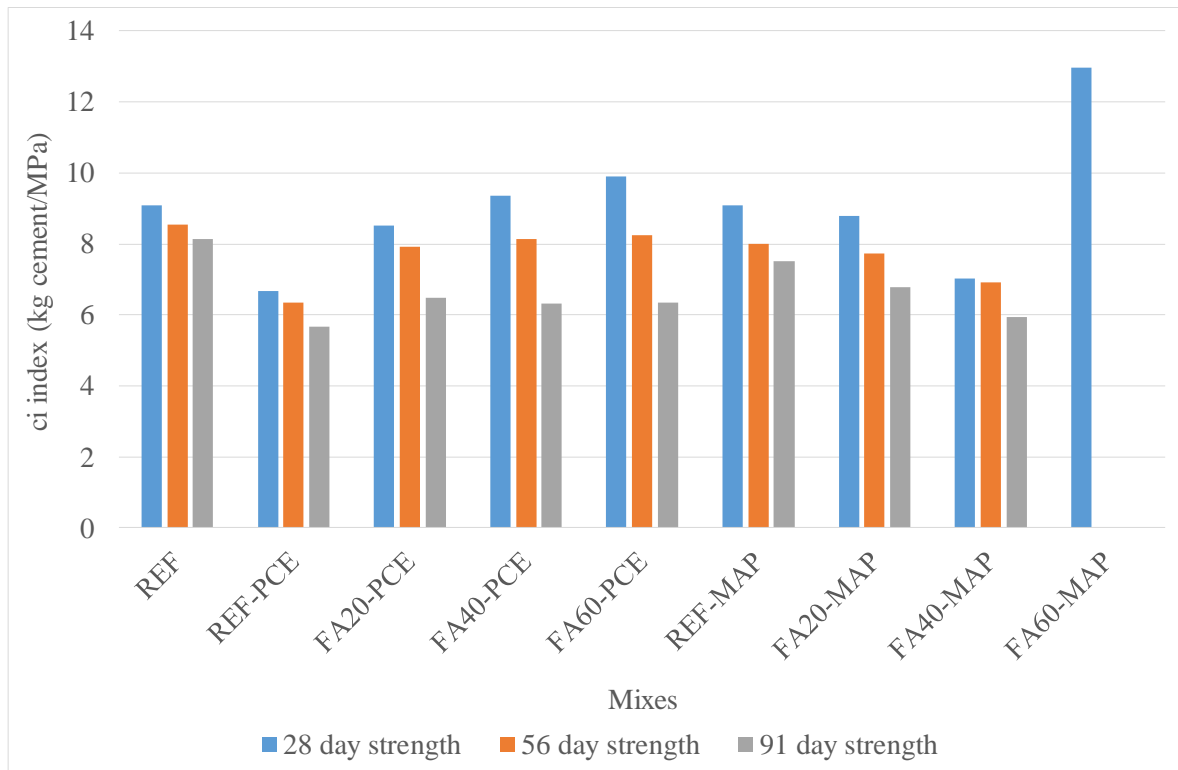
Figure 5.8: Ci indices of mixes containing superplasticisers
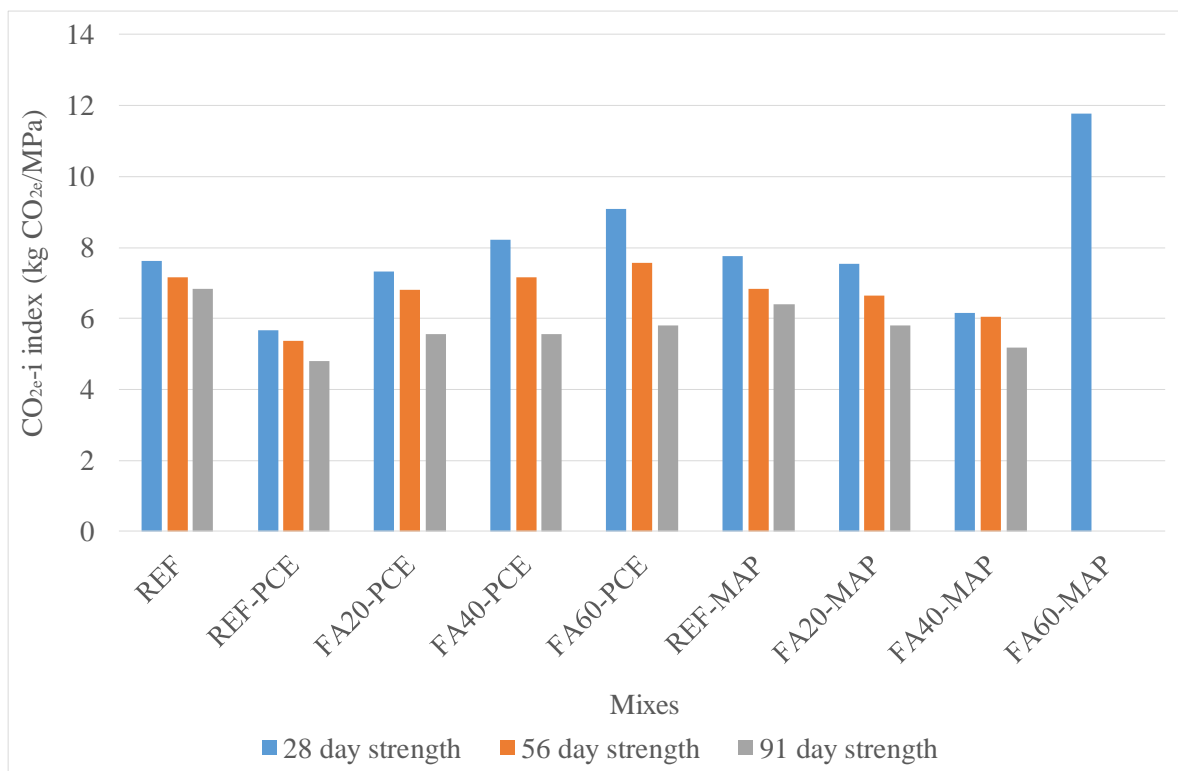
Figure 5.9: CO$_{2e}$-i indices of mixes containing superplasticisers
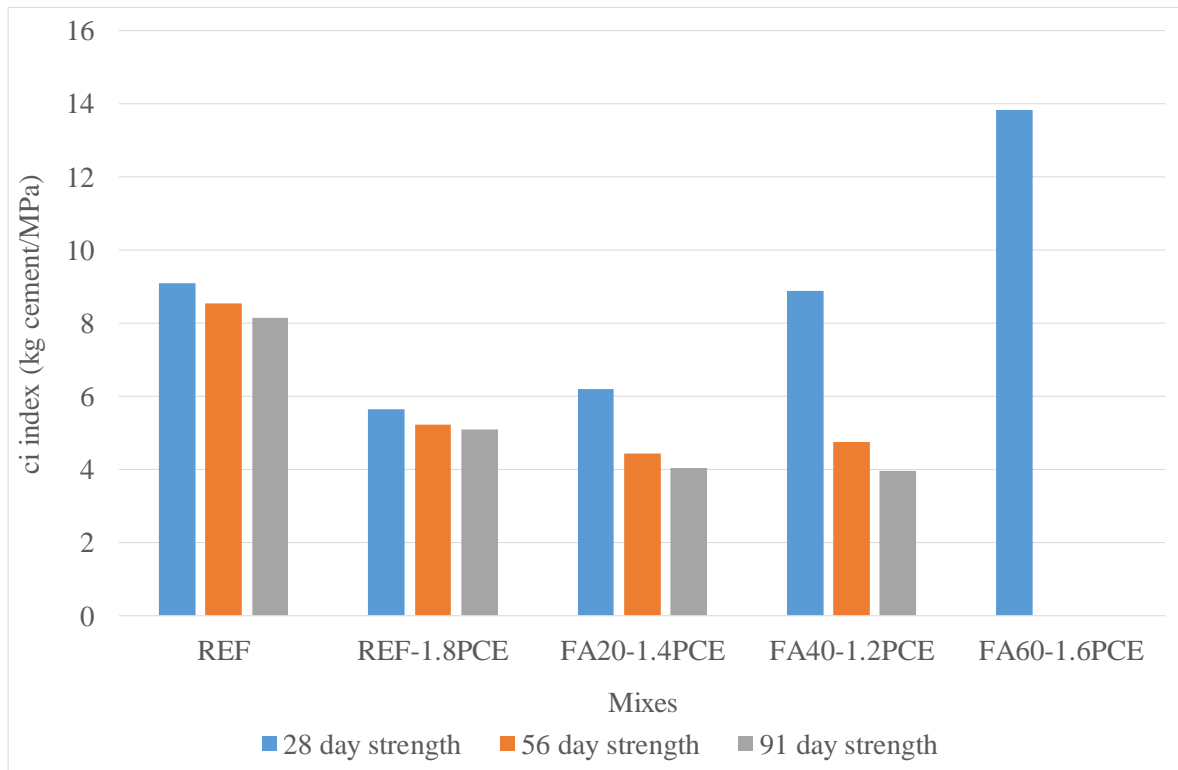
Figure 5.10: Ci indices of mixes containing double optimal dosage
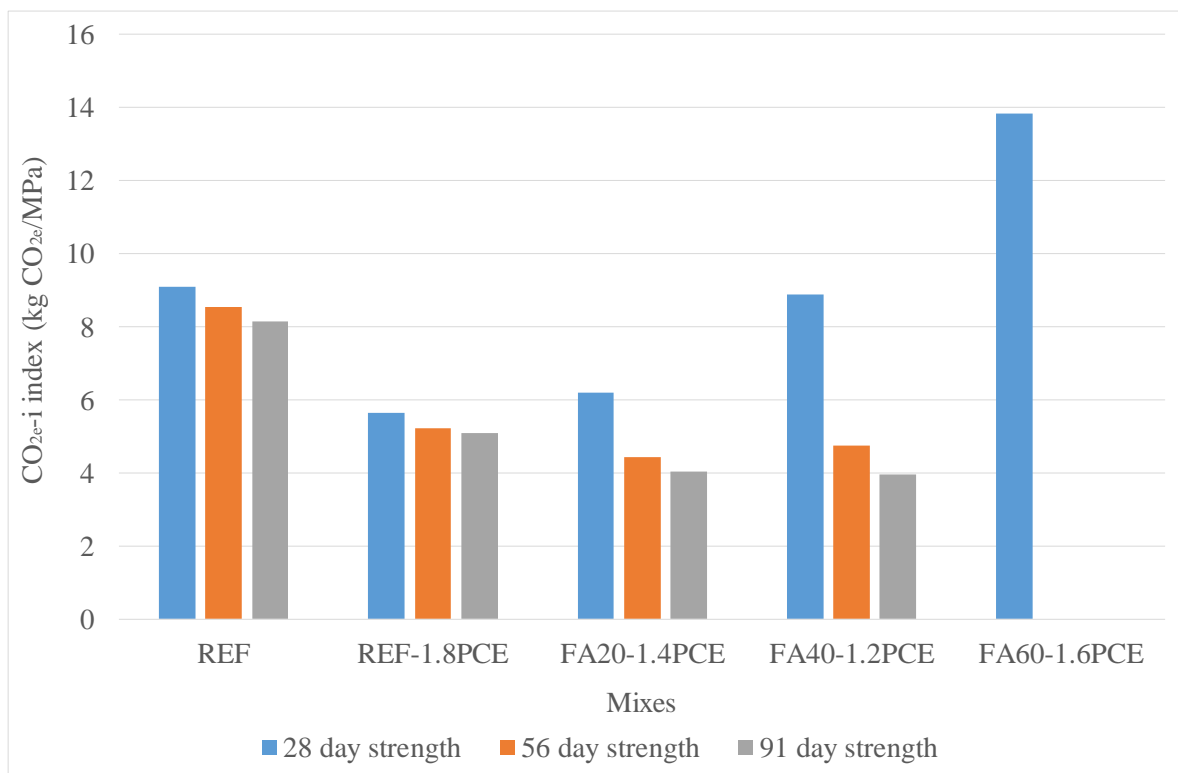
Figure 5.11: CO_{2e}-i indices of mixes containing double optimal dosage

The indices of the mixes with double the optimal dosage in certain instances vary greatly from those with the optimal dosage, providing a further increase in efficiency in terms of both the cement content and, subsequently, GWP. Especially without cement replacement and at a level of 20% the indices are improved at all ages. Furthermore, the later strength gain is again seen in further improvements, most dramatically for 40% cement replacement.

5.5   Concluding summary

This chapter described the development of mixes by the addition of two types of superplasticiser to the previously developed mixes, at constant slump and water/binder ratio. The superplasticiser was added at dosages determined using the Marsh cone test, and the suitability of this dosage evaluated by doubling it and determining the effect of this on the results. The mixes were subjected to tests of previously mentioned plastic and hardened properties.

Initially, it was found that developing mixes with double the optimal dosage proved difficult, as these were found to be very sensitive to even the smallest changes in water requirement. They furthermore proved to be highly sticky and viscous.

With regard to the rheological properties it was found that the superplasticisers at the Marsh cone dosage were effective in slightly increasing the viscosity and decreasing the yield stress of the mixes. Although doubling the dosage determined by the Marsh cone in mixes lowered their yield stress, it excessively increased their viscosity, more than tripling it, when compared to mixes with equivalent replacement levels. This made these mixes practically unworkable. The comparison of the MAP and PCE based superplasticisers was limited by the inadequate R^2 values of mixes containing MAP based superplasticiser. However, Mixes FA40-MAP and FA40-PCE showed that the MAP based superplasticiser showed better performance. Furthermore, mixes up to a replacement level of 40%, i.e. FA40-MAP, showed positive rheological qualities and are thus suitable for use in this regard.

The inclusion of superplasticisers negatively impacted the setting times of the mixes, delaying these considerably. Again, this effect was especially pronounced the greater the cement replacement level.

The compressive strength of the mixes was largely influenced negatively by the use of superplasticisers at the dosage determined by the Marsh cone. Again, with increasing replacement levels the strength decreased. The mixes with MAP based superplasticiser showed greater strengths than mixes with PCE based superplasticiser, at cement replacement levels of 20% and more. Particularly, mixes with a replacement level up to 40% were identified to have adequate strength and are therefore similarly recommended for further use. Doubling the dosage increased the strength of

the mixes. This again potentially shows that the superplasticiser targets and activates the cement, more so than fly ash.

The use of superplasticisers in the mixes made them less permeable than the equivalent reference mixes previously established, possibly due to the better dispersion of cement particles and the subsequent better homogeneity of the concrete. The acrylic based superplasticiser MAP functioned slightly better at higher replacement levels. A trend of decreased OPI values for increased cement replacement was observed, which could again indicate a particular interaction between and limited to the superplasticiser and cement. Doubling the dosage had no significant impact on the durability.

The GWP of the mixes was reduced significantly by the use of both superplasticisers. Compared to the equivalent reference mixes, reductions up to 20% were achieved, with higher cement replacement levels resulting in lower GWP. Doubling the dosage of superplasticiser caused a small further reduction of 5% at most, proving the validity of the Marsh cone results in this regard.

Finally, the c_i and $CO_{2e}\text{-}i$ indices of the mixes were determined. These were again found to follow the same trend due to the large contribution of cement to the GWP of the mixes. With the dosage determined by the Marsh cone, for higher replacement levels, mixed results were obtained at an age of 28 days due to the lower strength of these mixes compared to Mix REF and the equivalent reference Mixes FA20, FA40 and FA60. At later ages, the indices improved due to the strength gain compared to Mix REF. Both superplasticisers showed similar performance, with Mix FA40-MAP performing particularly well. Doubling the dosage showed a significant effect due to the minor reduction in GWP but major strength gains when this dosage was used.

In conclusion, a superplasticiser for use in the optimised mixes was selected based on the performance in these tests, and the validity of the Marsh cone test to establish an optimal dosage assessed. In the first regard, the MAP based superplasticiser was chosen, due to its better performance in a number of tests. Regarding the validity of the dosage established by the Marsh cone, the Marsh cone dosage can be described as optimal in most cases, as mixes with the Marsh cone dosage performed better in a number of tests. This motivates its choice. Mixes up to a 40% cement replacement level (i.e. FA40-MAP) showed potential.

An approach to similarly reduce the water requirement of concrete is the optimised fine aggregate particle packing of concrete. This is discussed in the following chapter.

Chapter 6

Cement Content Reduction by Fine Aggregate Particle Packing

This chapter focusses on the establishment of concrete mixes with a reduced water requirement due to optimised fine aggregate packing, and the subsequent binder-content reduction at a constant water/binder ratio. More specifically, this optimised fine aggregate particle packing was used for the mix designs previously established in Chapter 4, and new mix designs were devised. Firstly, the mix designs of said concrete mixes are presented and discussed. The results of tests of various plastic and hardened properties of these mixes are then shown and discussed separately. Subsequently, the sustainability properties of the mixes are elaborated on. Finally, a concluding summary is provided in order to again point out the most significant attributes of this range of concrete mixes.

6.1 Concrete mix designs

The mix designs of the mixes in which the fine aggregate was optimised can be seen in Table 6.1 and 6.2, for those mixes with SCM as a cement replacement, and those mixes with SCM and filler as a cement replacement respectively. Table 6.1 furthermore shows the reference mix design to enable simpler comparison. This approach was carried out for mixes of cement replacement levels up to 40%, as these performed well in Chapter 3.

The naming of the mixes is described in Section 3.4.4. It can be seen that the optimised particle packing of the fine aggregate fraction resulted in significant reductions of the water requirement, when comparing Mix REF-PP to Mix REF, and the other mixes to corresponding mixes without optimised particle packing. This could be a combination of the reduced volume of voids due to optimised particle packing, as well as the removal of dust from the sands when sieving. Again, for the mixes with SCM replacing cement, a reduced water requirement can be observed the higher the cement replacement level. For the mixes with SCM and filler as cement replacement, a slightly higher water requirement was observed for FA20GL10-PP than FA10GL10-PP. Although this might seem to be contradictory to the previously observed trends, comparing the reference mixes for the two, i.e. FA20GL10 and FA10GL10, a similar water requirement can be noticed, with FA20GL10 only requiring slightly less water.

The size range of the fine aggregate for these mixes, from 0.15 mm to 0.6 mm, was validated by the trial Mix REF-PP(1) seen in Table 6.3. As can be seen, the particle sizes used for the Fuller curve ranged from 0.075 to 0.6 mm for this mix, thus giving it a wider range than in the mixes shown in Table 6.1 and Table 6.2, with a finer fraction also included.

Table 6.1: Mix designs of reference mix, mixes with optimised particle packing and SCM

Mix		REF	REF-PP	FA20-PP	FA40-PP
Water (kg/m^3)		215	182	170	166
Cement (kg/m^3)		430	364	272	199
Fly ash (kg/m^3)		0	0	68	133
Fine sand (kg/m^3)	0.6 mm	358	178	184	184
	0.3 mm		141	146	146
	0.15 mm		109	113	113
Coarse sand (kg/m^3)	0.6 mm	358	178	184	184
	0.3 mm		141	146	146
	0.15 mm		109	113	113
Stone (kg/m^3)		1050	1050	1050	1050

Table 6.2: Mix designs of mixes with optimised particle packing, SCM and filler

Mix		FA10GL10-PP	FA20GL10-PP
Water (kg/m^3)		170	173
Cement (kg/m^3)		272	243
Fly ash (kg/m^3)		34	69
Limestone (kg/m^3)		34	35
Fine sand (kg/m^3)	0.6 mm	185	180
	0.3 mm	147	143
	0.15 mm	114	111
Coarse sand (kg/m^3)	0.6 mm	185	180
	0.3 mm	147	143
	0.15 mm	114	111
Stone (kg/m^3)		1050	1050

Table 6.3: Validation of mixes with optimised particle packing

Mix		REF-PP(1)
Water (kg/m^3)		208
Cement (kg/m^3)		416
Fly ash (kg/m^3)		0
Fine sand (kg/m^3)	0.6 mm	131
	0.3 mm	104
	0.15 mm	81
	0.075 mm	63
Coarse sand (kg/m^3)	0.6 mm	131
	0.3 mm	104
	0.15 mm	81
	0.075 mm	63
Stone (kg/m^3)		1050

Comparing Mixes REF-PP(1) with REF(PP) reveals the higher water requirement of the former at the same slump as the latter. This firstly indicates that the inclusion of the finer fraction may not be beneficial towards the reduction of water requirement and ultimately binder content, and it was thus omitted from the final mixes. Secondly, this indicates that the finer aggregate, i.e. sand, have a greater influence on the water requirement than the coarser aggregate, i.e. stone. It is thus of primary importance to optimise the particle packing of the former, as done throughout the rest of this section.

6.2   Plastic properties of concrete

This section focusses on the results of the tests on the concrete in its plastic state. Firstly, the consistency, and certain properties as part of this, of all mixes is elaborated on. Following this, results of the rheological tests on these mixes are given. Finally, results of the setting time tests are shown.

6.2.1   Consistency

The aspects that were evaluated as part of consistency were the slump, segregation and general uniformity of the mixes. The slump test confirmed that all mixes showed a slump of 100 ± 10 mm. The assessments of segregation and general uniformity were carried out visually. All mixes in this section showed no signs of segregation and were generally found to be uniform to an even greater extent than previous mixes, most probably due to the optimal particle packing of the fine aggregate.

6.2.2   Rheology

The results of the flow curve test on these mixes, as well as Mix REF, 10 minutes after mixing, can be seen in Figure 6.1. The stress growth test again yielded inaccurate results, and the plastic viscosity and dynamic yield stress data obtained in the flow curve test was used. However, the majority of the mixes showed insufficient R^2 values, possibly due to the accumulation of the large aggregate and the rotating vane getting stuck, thus increasing the measured values of torque and distorting the data. These mixes thus have to be interpreted carefully.

Nonetheless, the comparison of Mixes REF and REF-PP, both with sufficient R^2 values, proves to be interesting. It can be seen that the improved particle packing of Mix REF resulted in a mix with higher viscosity and a relatively small increase in yield stress, namely REF-PP. This proves to be promising, as it implies that the application of particle packing to a mix at constant slump makes that mix less prone to segregation, due to an increased viscosity, but not excessively sticky, as experienced during the inclusion of superplasticisers. Similarly, the only slight increases in yield stress between Mixes REF and REF-PP indicate a good consistency of mixes with optimised particle packing, even with a greatly reduced water content. Although these findings can not be confirmed for the other mixes due to their statistical insignificance, these observations on their own could prove valuable.
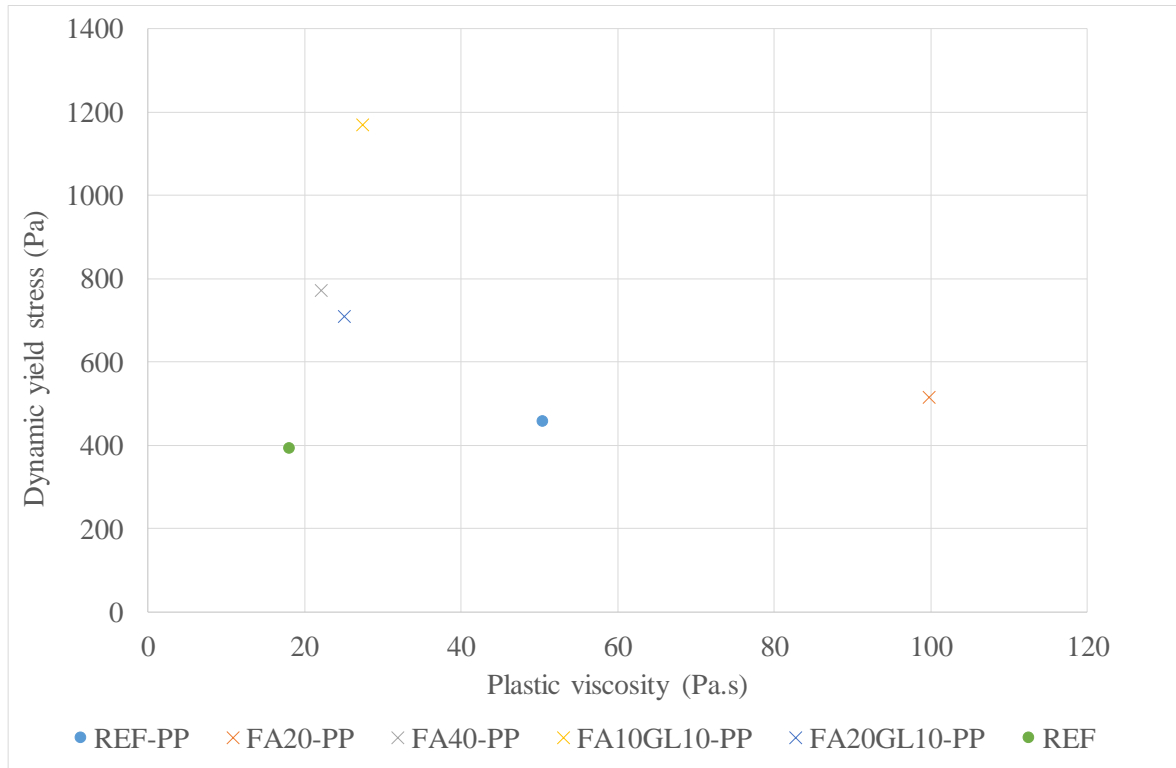
Figure 6.1: Yield stress and plastic viscosity of mixes with optimised particle packing

6.2.3   Setting time

The results of the setting times test can be seen in Figure 6.2. It must be noted that the initial and final setting times of all mixes were normalised according to those of the Mix REF, which has an initial setting time of 330 min and a final setting time of 410 min.

When comparing the setting times of the mixes in Figure 6.2 to the corresponding mixes without optimised particle packing in Figure 4.1, it can be seen that the optimised particle packing results in shorter initial and final setting times. This could be explained by the decrease in voids in the mix, which implies that cement particles are closer to each other. They can thus form bonds more easily and quickly, causing the setting time to decrease.

Again, the trend of greater setting times for mixes with greater replacement levels of cement by fly ash and ground limestone is observed. Furthermore, the limestone again does not seem to accelerate the setting of the concrete mixes, as can be seen when comparing mixes FA20-PP and FA10GL10-PP.
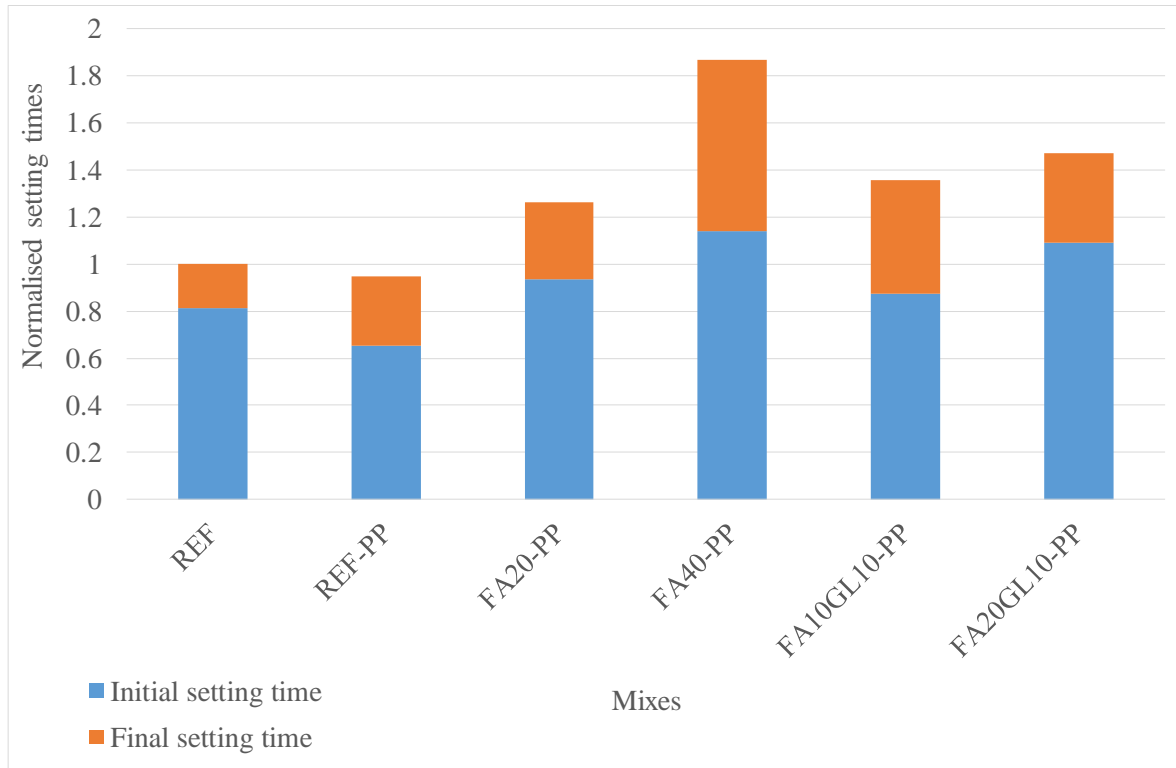
Figure 6.2: Normalised setting times of reference mix, mixes with optimised particle packing

6.3 Hardened properties of concrete

The results of the tests on the concrete mixes in their hardened state are provided in this section. Firstly, the results of the compressive strength tests are given. This is followed by the results of the OPI test.

6.3.1 Compressive strength

The compressive strength of the mixes and the Mix REF can be seen in Figure 6.3. The optimisation of the fine aggregate particle packing resulted in similar to higher strengths at all ages when comparing the mixes to reference mixes with equivalent cement replacement levels. This could be due to the fact that water is less likely to be caught in voids, as their volume has been reduced due to the optimised particle packing. This in turn causes more water to be available for the hydration reaction, thereby accelerating and intensifying it. All mixes reach a strength of around 40 MPa at 28 days.

Again, the mixes with fly ash show significant strength gains at later ages when compared to mix REF and REF-PP. Particularly Mix FA20-PP is effective in this regard. The larger the fraction of cement that is replaced, the lower the strength.
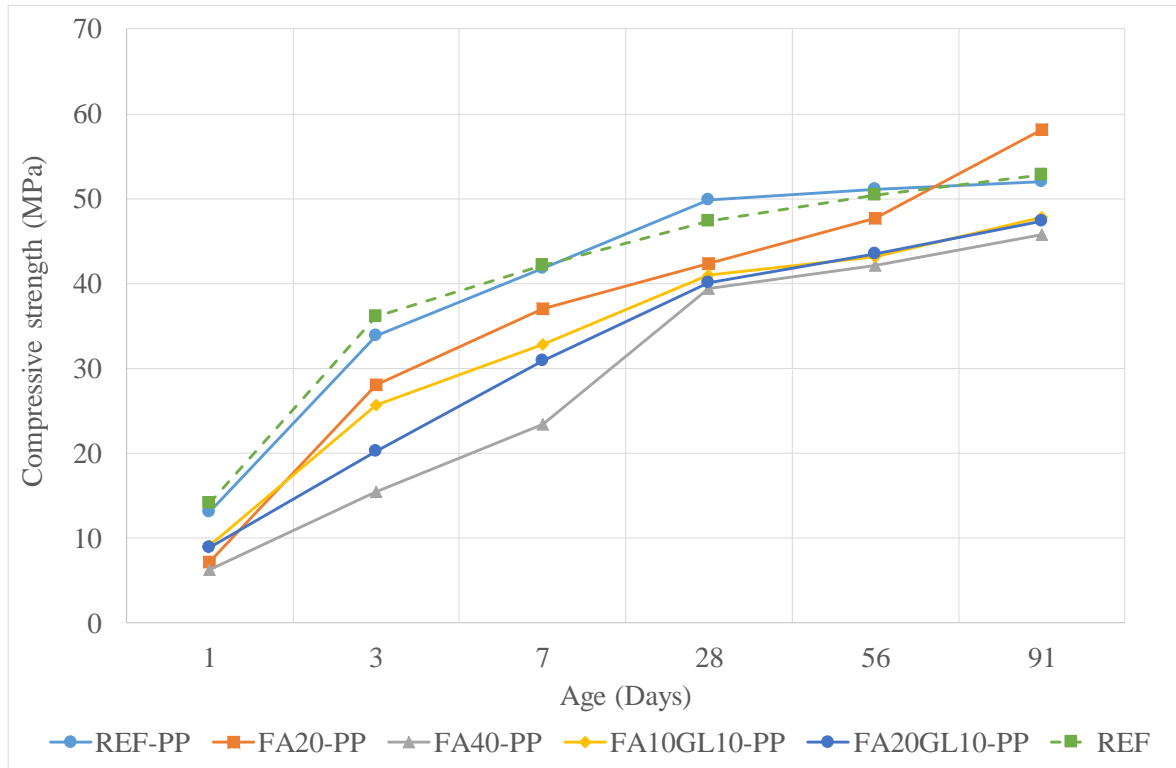
Figure 6.3: Compressive strength of mixes with optimised fine aggregate particle packing

6.3.2   Durability

The OPI values of the respective concrete mixes, along with that of the Mix REF, can be seen in Table 6.4. All values can be classified as "good" or "excellent" according to Table 3.9.

Table 6.4: OPI values of reference mix, mixes with optimised particle packing

Mix	REF	REF-PP	FA20-PP	FA40-PP	FA10GL10-PP	FA20GL10-PP
OPI value	9.68	9.73	9.96	10.41	10.13	10.2

When comparing the corresponding mixes in Table 6.4 and Table 4.3, it can be observed that the optimisation of particle packing has a positive influence on durability, as all OPI values of mixes with optimised particle packing are higher than their counterparts without optimised particle packing. This can again be attributed to the smaller volume of voids in the concrete mixes when particle packing is optimised. Due to this, it is more difficult for substances to permeate through the concrete, resulting in lower permeability overall. Furthermore it is again observed that the addition of fly ash and ground limestone has a positive influence on the durability of concrete, as the OPI values increase the larger the fraction of cement that is replaced by the two materials.

6.4   Sustainability study

This section lays out the results of the sustainability studies conducted for the mixes. In terms of this, their equivalent CO_2 emissions and the binder and carbon dioxide intensity indices are presented.

6.4.1   Carbon emissions study

The Greenhouse Warming Potential (GWP) established as part of the carbon emissions study on the mixes can be seen in Figure 6.4. This was normalised according to Mix REF, which has a GWP of 361 kg CO_{2e}/m^3 concrete . Again, the majority of the GWP of all mixes is due to cement. The impact that optimised fine aggregate particle packing has on the reduction of water requirement, and subsequently binder content, is displayed by the GWP of the mixes. As the cement and total binder content reduces, so does the GWP of the mixes, with those mixes with higher cement replacement levels again displaying the lowest values. When comparing these mixes to their equivalent reference mixes, reductions in GWP ranging from 8 to 15% can be seen, with reductions becoming less pronounced at higher cement replacement levels. Again, at the same cement replacement level, mixes with fly ash, and mixes with fly ash and limestone exhibited a similar reduction in GWP (e.g. FA20-PP and FA10GL10-PP). Optimising the particle packing of the fine aggregate thus proves to be efficient in reducing the GWP of concrete mixes.
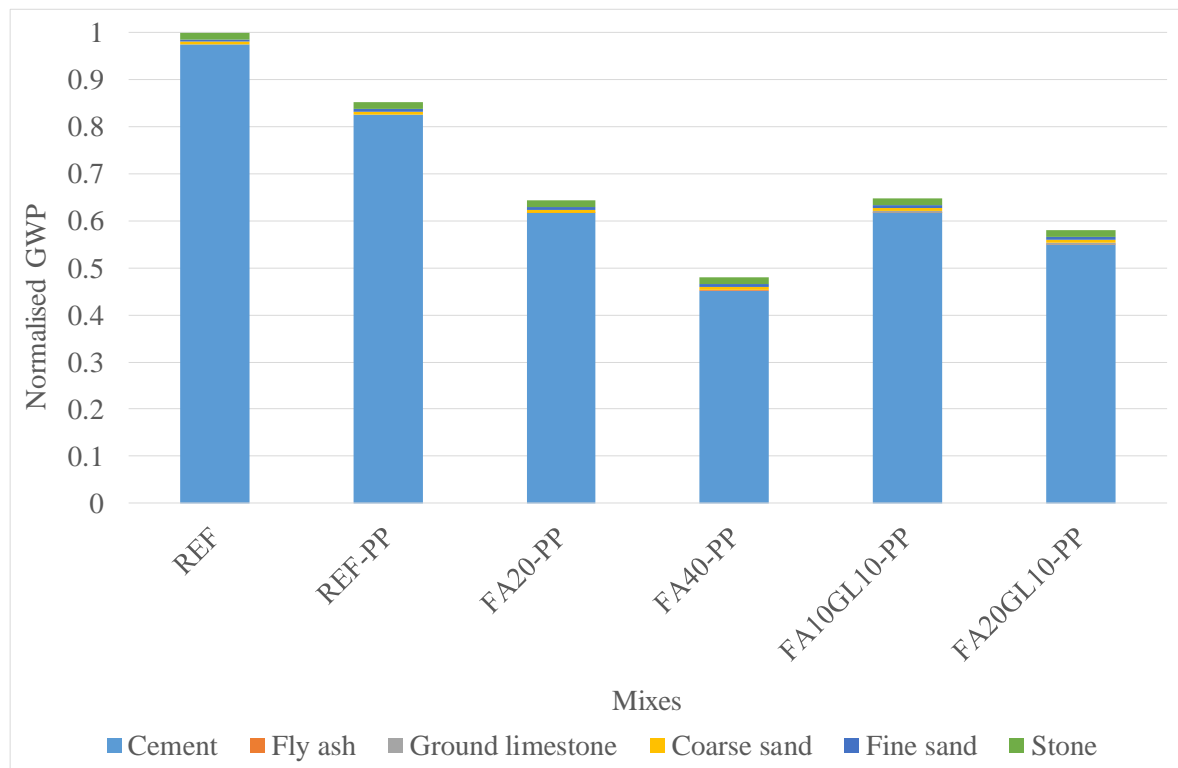
Figure 6.4: Normalised GWP of mixes with optimised particle packing

6.4.2   Cement and carbon dioxide intensity index

The cement intensity (ci) and carbon dioxide intensity (CO_{2e}-i) indices of these mixes can be seen in Figures 6.5 and 6.6. These follow the same trend due to the large contribution of cement to the GWP of the mixes.

The optimisation of fine aggregate particle packing improves both indices greatly for all mixes, when comparing these to mix REF and their respective equivalent mixes. The improvements are especially prominent at later ages, due to improved compressive strength at these ages. Mixes FA10GL10-PP and FA20-PP, both with 20% cement replacement, show similar reductions of the indices, showing the similar capabilities of both fly ash and limestone. The greater the fraction of cement replaced, the lower the indices and the more suitable the mixes in this regard.
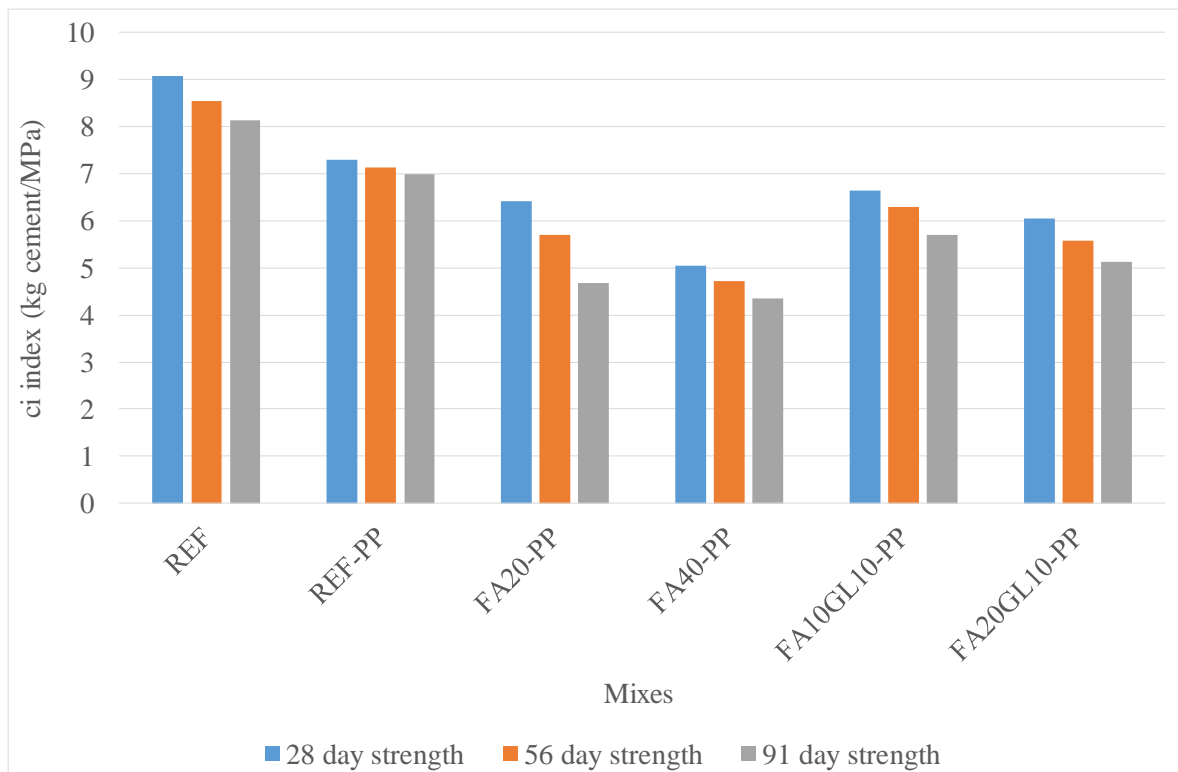
Figure 6.5: ci indices of mixes with optimised particle packing
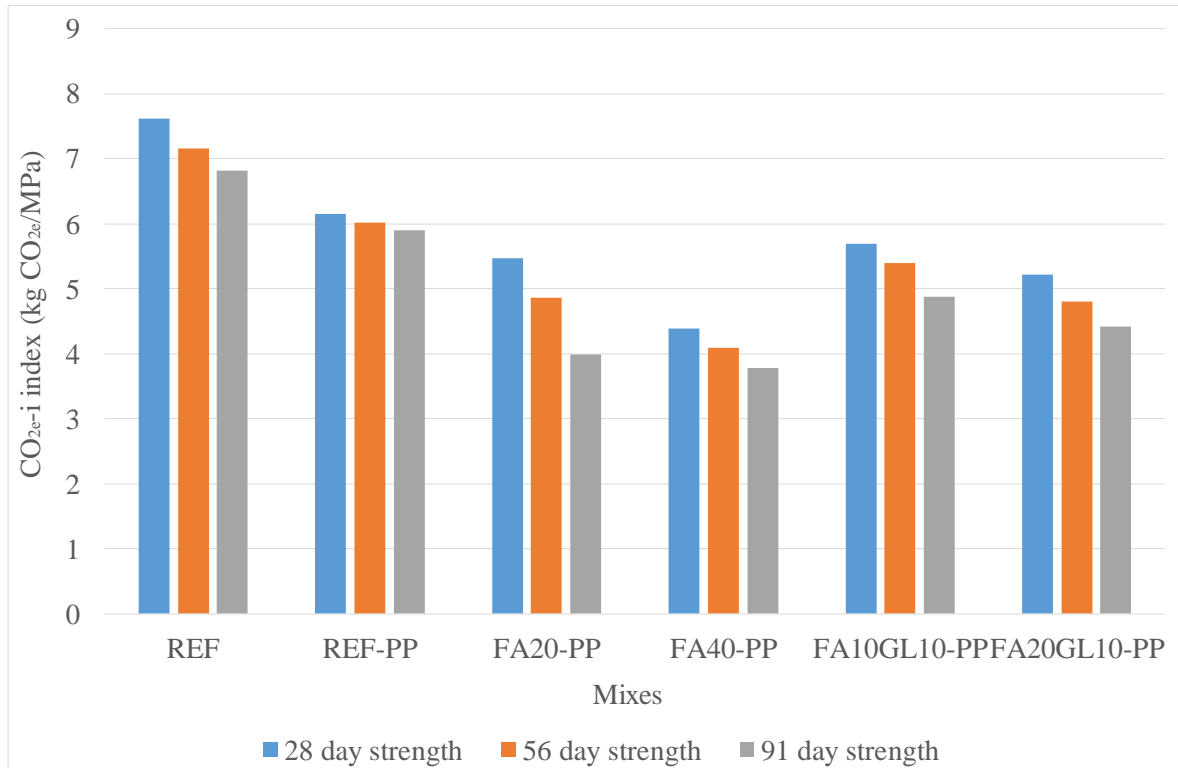
Figure 6.6: CO$_{2e}$-i indices of mixes with optimised particle packing

6.5   Concluding summary

This chapter described the reduction in water requirement of the mixes by means of the optimisation of the fine aggregate fractions of selected mixes established in Chapter 3. It was found that the water requirement could be greatly reduced by particle packing. However, this could partially also be due to the removal of dust from the fine aggregate fraction. The mixes were subjected to the previously mentioned tests of plastic and hardened properties.

With regard to rheological properties, the investigation was limited by the inadequate R^2 values of the majority of the mixes. However, Mixes REF and REF-PP, with adequate R^2 values, revealed a moderate increase in plastic viscosity at similar yield stresses, resulting in a lesser chance of segregation without excessive stickiness of the mix and similar consistencies of the mixes. The optimisation of fine aggregate thus results in improved rheological properties for these mixes.

The optimisation of fine aggregate particle packing resulted in a reduced setting time for all mixes, when compared with mixes with the equivalent cement replacement, without optimised particle packing. This is possibly due to the decrease in voids in the concretes structure and the ensuing closer distances between the cement particles, accelerating the reactions between these.

The compressive strengths were influenced positively by the optimisation of fine aggregate particle packing. All mixes reached similar or higher strengths at all ages, when compared to their counterparts without optimised particle packing. Particularly at later ages, the fly ash in the mixes causes substantial strength gains when compared to Mix REF-PP, with all mixes reaching strengths in excess of 40 MPa. This approach is therefore useful for all replacement levels shown in this section.

In terms of durability, the optimisation of the fine aggregate particle packing showed a positive influence, by reducing the permeability of all mixes compared to their equivalent reference mixes. Mixes with higher fly ash contents again had higher OPI values This further validates the use of this technique, and the choice of the mixes for which it was used.

As part of the sustainability study, the GWP of the mixes were established. The mixes in this section showed a pronounced reduction of the GWP when compared to their equivalent reference mixes without optimised particle packing. Greater fractions of cement replacement again result in lower GWP.

Lastly, the ci and CO_{2e}-i indices were determined and the efficiency of these mixes in terms of cement used and GWP produced per unit of strength assessed. The two indices again followed the same trend due to the large influence of the cement on the GWP. The combination of the positive influence that the optimisation of particle packing has on the cement content and GWP, as well as the compressive strength, cause the indices to be improved greatly. This is especially valid at later ages and higher cement replacement levels, at which additional improvements of these indices are seen.

It can be concluded that the use of particle packing optimisation of the fine aggregate caused vast benefits for the majority of properties of the mixes. Although a basic and practically applicable method was used, the benefits of this were pronounced in most tests. While this could not absolutely be ascertained during the rheological tests, in which the benefits could not be quantified for all mixes, all measured properties were improved. Furthermore, the mixes for which fine aggregate particle packing was optimised were also validated for further use, with a cement replacement level up to 40% (i.e. Mix FA40-PP) showing good results.

This leads to the inclusion of this approach, along with the other two, in the development of the final optimal mixes as discussed in the following chapter.

Chapter 7

Concrete Mixes with Optimised Cement Content

This chapter presents the concrete mixes established through the consolidation of the knowledge on the cement-content reduction in concrete, gained in Chapters 4 to 6. The term "optimised mixes" used in this section mostly refers to the cement contents of these mixes, as these were lowered to the greatest extent possible using the previously seen approaches. In this chapter, firstly, the mix designs that were established based on the initial workability requirement are shown and discussed. Following this, the results of the tests of the plastic and hardened properties of the concrete mixes are presented and discussed separately. Subsequently, the sustainability properties of the concrete mixes are reported on and discussed. Finally, a concluding summary, once again discussing the most important aspects of this range of mixes, is provided.

7.1   Concrete mix designs

The mix designs of the optimised mixes, incorporating all techniques used to lower the binder content at a constant slump, can be seen in Table 7.1. Furthermore, the reference mix REF is also provided, in order to enable a comparison between the mixes. The choice of cement replacement fractions, i.e. 20% to 40% of cement, were made based on their performance, as discussed in Chapter 4 and Chapter 6. The acrylic polymer (MAP) based superplasticiser was chosen, as discussed in Chapter 5.

Table 7.1: Mix designs of reference mix, optimised mixes

Mix		REF	FA20-PP-MAP	FA40-PP-MAP	FA10GL10-PP-MAP	FA20GL10-PP-MAP
Water (kg/m³)		215	135	138	143	141
Cement (kg/m³)		430	216	166	229	198
Fly ash (kg/m³)		0	54	110	29	56
Limestone (kg/m³)		0	0	0	29	28
Fine sand (kg/m³)	**0.6 mm**		216	210	209	210
	0.3 mm	358	172	167	167	167
	0.15 mm		133	129	129	129
Coarse sand (kg/m³)	**0.6 mm**		216	210	209	210
	0.3 mm	358	172	167	167	167
	0.15 mm		133	129	129	129
Stone (kg/m³)		1050	1050	1050	1050	1050
MAP Superplasticiser (kg/m³)		-	1.62	1.38	1.69	1.72

Section 3.4.4 explains the naming of the mixes. Firstly, comparing the optimised mixes to Mix REF, it can be seen that the water requirement and, subsequently, cement content were drastically reduced

throughout the course of this investigation. Effectively, for all of the optimised mixes except for Mix FA10GL10-PP-MAP, the cement content was halved while a constant slump was maintained. Furthermore, it is observed that the proportion of cement that was replaced by an SCM or filler no longer influences the water requirement as observed earlier on in the investigation. In essence all mixes showed a similar water requirement, regardless of the percentage of cement that is replaced. This could be attributed to the fact that at extremely low cement contents and, correspondingly, higher sand contents in the mix, the water requirement is governed by the sand content to a large extent. This again makes optimised particle packing of the sand extremely valuable.

7.2   Plastic properties of concrete

In this section the results of the tests on the concrete in its plastic state are provided. Firstly, the consistency of the mixes is elaborated on. Subsequently, results of the rheological tests are provided. Finally, results of the setting time tests are given.

7.2.1   Consistency

Aspects of consistency that were considered are the slump, segregation and general uniformity of the mixes. Regarding the slump, the slump test carried out on all mixes confirmed a value of 100±10 mm for all mixes. Furthermore, it was confirmed that the mixes showed no segregation, and were generally uniform. In this regard, the improved particle packing was noticeable again, providing consistent and uniform concrete mixes throughout.

7.2.2   Rheology

The results of the flow curve test on the optimised mixes, as well as Mix REF 10 minutes after mixing, can be seen in Figure 7.1. All mixes showed adequate values of R^2 and the results can thus be considered reliable.

When interpreting these results certain successes were obtained in terms of the optimisation of the rheology of the mixes. Mixes FA40-PP-MAP and FA10GL10-PP-MAP exhibit the most favourable properties, due to their slightly increased plastic viscosity, and subsequent increased resistance to segregation without the stickiness seen in the mixes containing superplasticiser. Mix FA20-PP-MAP fared slightly poorer in this regard, showing an almost excessive increase in viscosity, although not as pronounced as experienced during the inclusion of superplasticisers previously. Mix FA20GL10-PP-MAP showed a decrease in plastic viscosity. Overall, the increases in viscosity are less pronounced than those seen during the addition of superplasticiser (Figure 5.1) but more pronounced than the initial reference mixes in Figure 4.1. The mixes therefore have desirable rheological properties in this regard.

However, Mix FA20-PP-MAP, along with mixes FA40-PP-MAP and FA20GL10-PP-MAP, also exhibited an increased dynamic yield stress, which potentially affects their workability negatively. Again, these higher levels of fly ash as a cement replacement cause a relatively larger increase in yield stress. However, this increase in yield stress is far less pronounced than during the substitution of cement by fly ash in particular, as seen in Figure 4.1. This suggests that the concurrent use of superplasticisers and optimal particle packing did indeed cause certain improvements in the rheology of the mixes, when compared to Mix REF and the initial reference mixes using fly ash and limestone as a cement replacement. This is particularly remarkable due to the greatly reduced water content of these mixes when compared to the initial mixes.
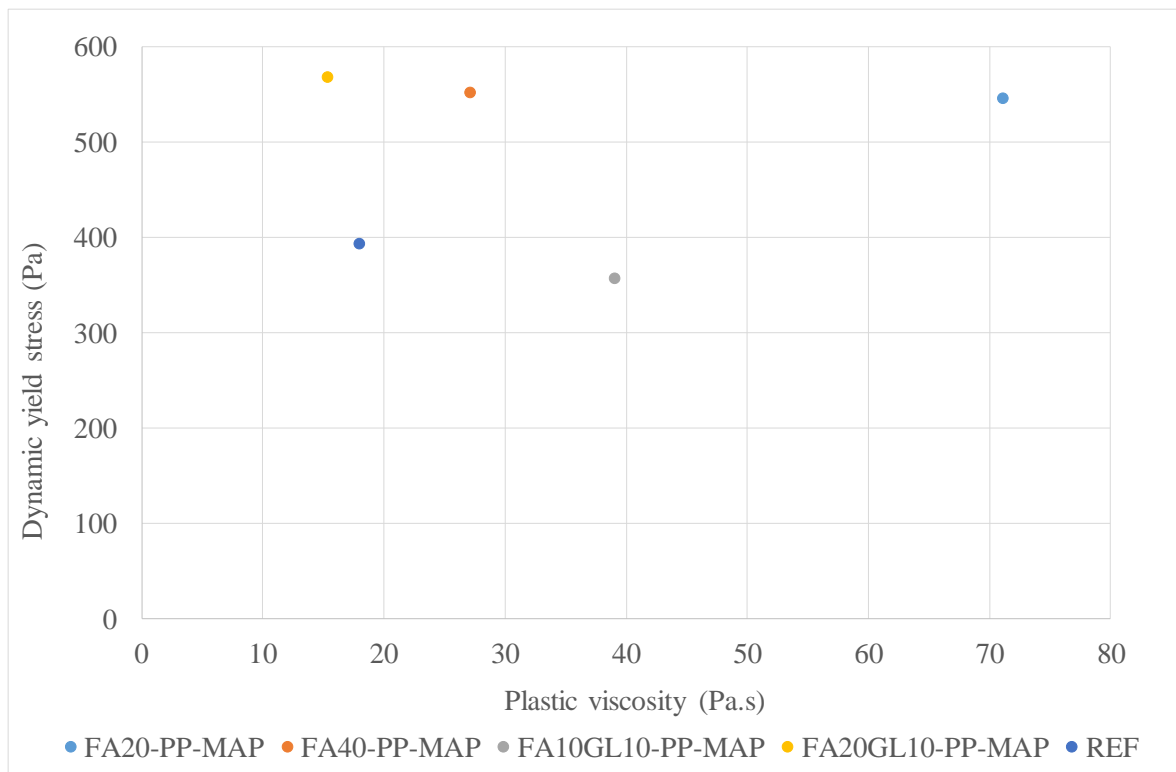
Figure 7.1: Yield stress and plastic viscosity of optimised mixes

7.2.3   Setting times

The results of the setting time tests can be seen in Figure 7.2, and are normalised according to the Mix REF, which is also shown in the figure. The initial setting time of Mix REF was 330 min, while its final setting time was 410 min.

From these results it can be seen that although setting times are delayed for the optimised mixes when compared to the reference mix, this delay is not as extreme as could be expected with the

simultaneous replacement of substantial fractions of cement and use of superplasticiser. This can be seen when comparing the results in Figure 7.2 with those in Figure 6.2, i.e. the mixes with the same replacement fraction of cement and the superplasticiser used in the optimised mixes. For instance, Mix FA40-PP-MAP has a shorter setting time than both FA40 and FA40-MAP. This shows that the setting time has been improved in the optimised mixes. This can most likely be attributed to the optimisation of particle packing negating the effects of the superplasticiser inclusion and cement replacement, causing all mixes to be well within practical bounds in this regard. However, it can again be noted that the inclusion of limestone did not have an accelerating impact on the setting time.
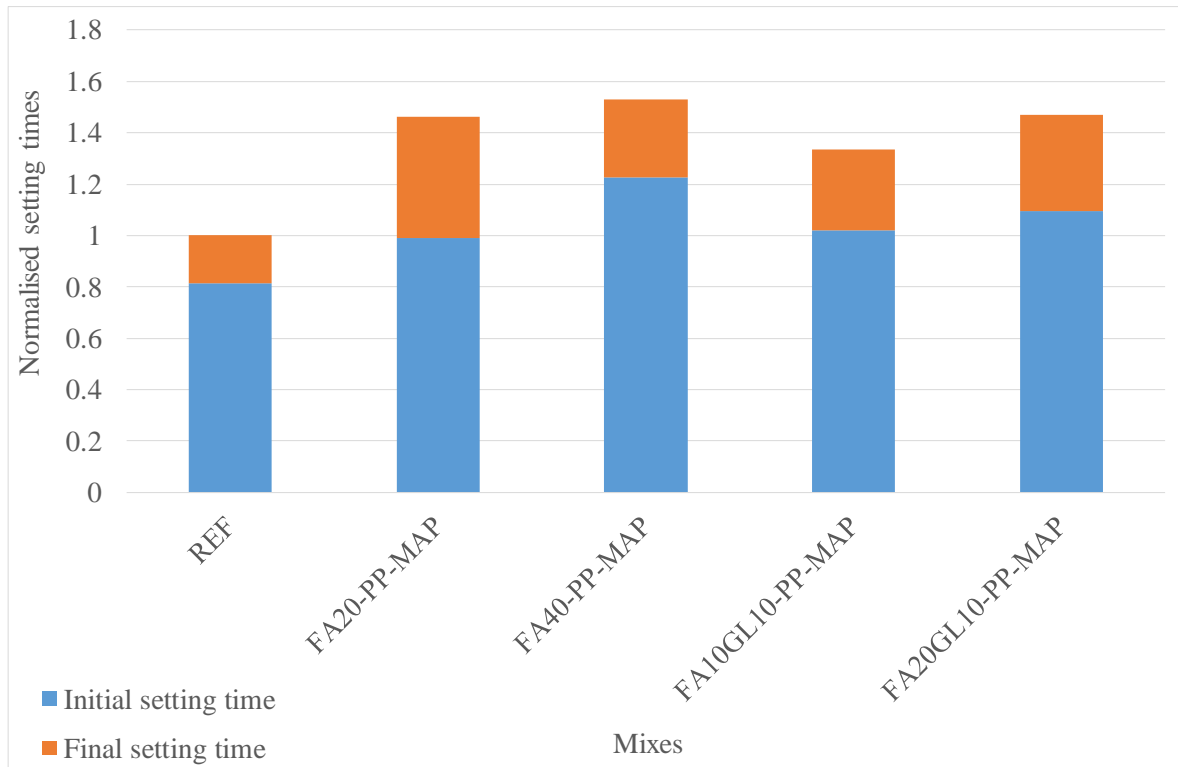
Figure 7.2: Normalised setting times of reference mix and optimised mixes

7.3   Hardened properties of concrete

This section provides the results of the tests on the concrete mixes in their hardened state. Firstly the results of the compressive strength tests are provided, followed by the results of the OPI tests.

7.3.1   Compressive strengths

The compressive strengths of the optimised mixes, as well as Mix REF, can be seen in Figure 7.3. When initially analysing these results, it can be seen that the strength development of Mixes FA10GL10-PP-MAP and FA20GL10-PP-MAP does not follow the conventional strength

development of concrete, as illustrated by Mix REF for instance. The former mixes show a decrease in strength between 28 and 56 days, before their strengths recover at 91 days.

With regard to the early age strength of the concrete, the low cement contents of the optimised mixes can be noticed by their low, or insignificant one day strengths. The mixes with 30 or 40% cement replacement, i.e. FA20GL10-PP-MAP and FA40-PP-MAP have particularly low strengths. However, this improves after 7 days, and all mixes show significant improvements until 28 days, with the exception of FA20-PP-MAP. The compressive strength of the latter mix stagnates between 7 and 28 days, with no reason found for this behaviour. The compressive strengths of between 22 and 27 MPa lead to the classification of these mixes as being able for use as "reinforced concrete with dense aggregate" (Roberts & Marshall, 2010). Nonetheless, they are significantly less than the compressive strength of Mix REF at 28 days.
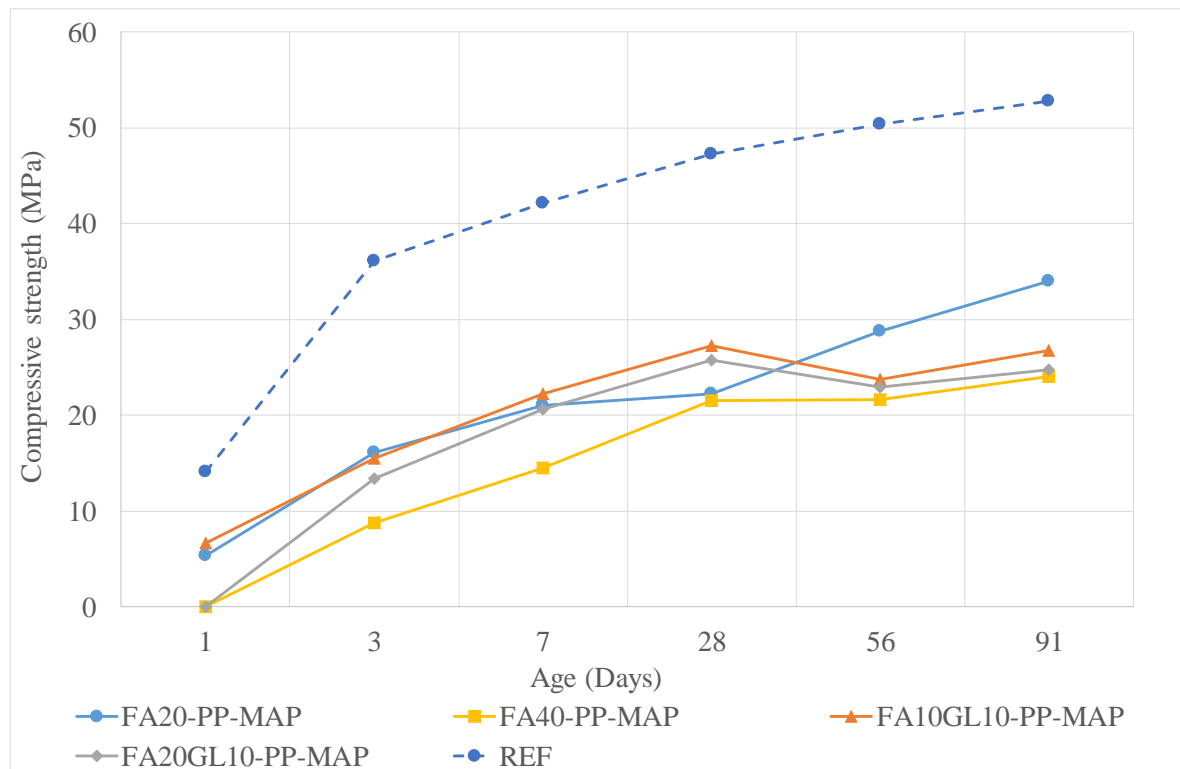
Figure 7.3: Compressive strengths of optimised mixes

Between ages 28 and 91 days, the compressive strength of all mixes except one stagnate or only show a slight improvement. Mix FA20-PP-MAP shows significant improvements of strength between 28 and 91 days, possibly due to the fly ash developing strength at these later ages. No explanation can be found as to why this behaviour was not observed in the other mixes. Finally, it can again be seen

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that the strength decreases the more cement is replaced with fly ash and limestone. However, all mixes could be classified as medium strength concretes after 91 days.

7.3.2 Durability

Table 7.2 shows the OPI values of the mixes obtained during the OPI test. All values can be classified as "good" according to Table 3.9, thus meaning that the optimised mixes are sufficiently impermeable and durable in this regard.

Table 7.2: OPI values of reference mix, optimised mixes

Mix	REF	FA20-PP-MAP	FA40-PP-MAP	FA10GL10-PP-MAP	FA20GL10-PP-MAP
OPI value	9.68	9.93	9.87	9.6	9.74

As can be seen from these results, all mixes except Mix FA10GL10-PP-MAP can be classified as more durable than the reference Mix REF in terms of impermeability. Both mixes with only fly ash as cement replacement have similar OPI values, suggesting that at certain, low binder contents larger cement replacement fractions by fly ash no longer result in greater impermeability. Although the mixes with fly ash and ground limestone are still sufficiently durable, they are again more permeable than their counterparts with only fly ash as a cement replacement. This makes fly ash the more favourable material to use in the permeability aspect of durability.

7.4 Sustainability study

The results of the investigation of the sustainability properties of the mixes are presented in this section. Firstly, the equivalent CO_2 emissions of the mixes are presented. Following this, the binder and carbon dioxide intensity indices of the mixes are shown.

7.4.1 Carbon emission study

The carbon emission study entailed establishing the Greenhouse Warming Potential (GWP) of the mixes. The results of this study on the optimised mixes can be seen in Figure 7.4. The GWPs of the mixes were normalised according to that of the Mix REF, namely 361 kg CO_{2e}/m^3 concrete.

As can be seen from the optimised mixes, the combination of all techniques to both replace and reduce the cement content substantially impacted the GWP. When comparing the original Mix REF to these optimised mixes, a reduction in GWP of 45% to 60% was achieved, or when expressed absolutely, 162.45 to 216 kg CO_{2e}/m^3 concrete. Again, the size of the fraction of cement that is replaced has the biggest impact on the GWP, with Mix FA40-PP-MAP having the lowest GWP and the largest fraction of cement replaced. Mixes with the same fraction of cement replaced, i.e. FA20-

PP-MAP and FA10GL10-PP-MAP, have similar GWPs. Overall, the difference in GWP between the mixes has decreased. Where Mixes FA20 and FA40 showed a 20% difference compared to Mix REF, this changed to about 10% for Mixes FA20-PP-MAP and FA40-PP-MAP. It is therefore likely that a limit as to the possible reduction exists, and that the optimised mixes are within the range of this limit. The combination of the techniques to reduce the cement content could therefore be deemed successful.
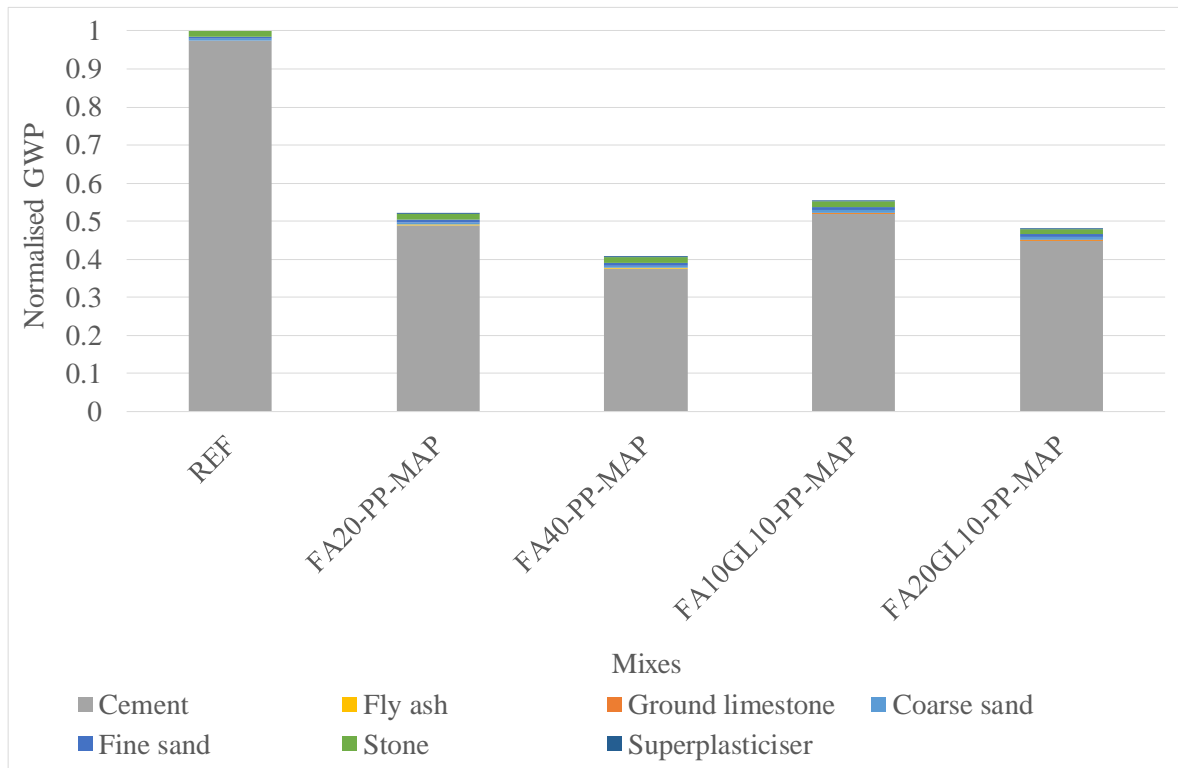
Figure 7.4: Normalised GWP of optimised mixes

7.4.2   Cement and carbon dioxide intensity index

The cement intensity (ci) and carbon dioxide intensity (CO_{2e}-i) indices of the optimised mixes and Mix REF can be seen in Figures 7.5 and 7.6. The two indices follow the same trend due to the large contribution the cement has towards the GWP of the mixes, while the contributions of the other materials are relatively small.
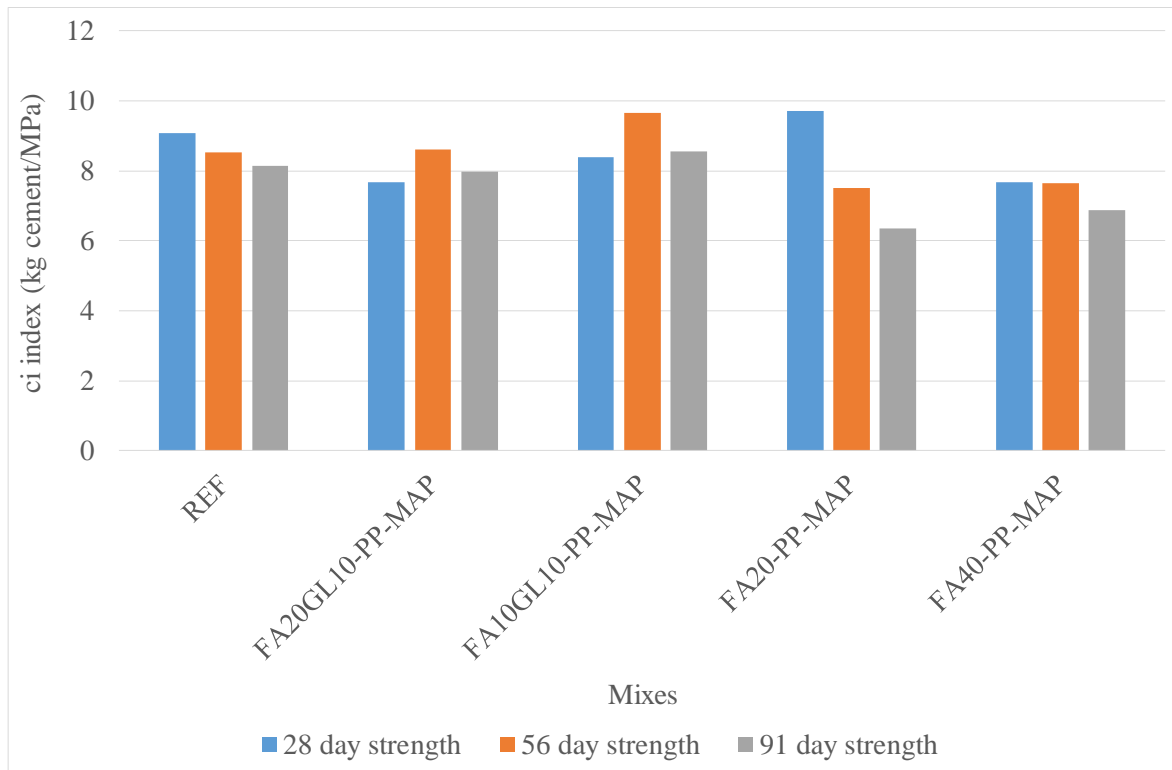
Figure 7.5: ci indices of optimised mixes
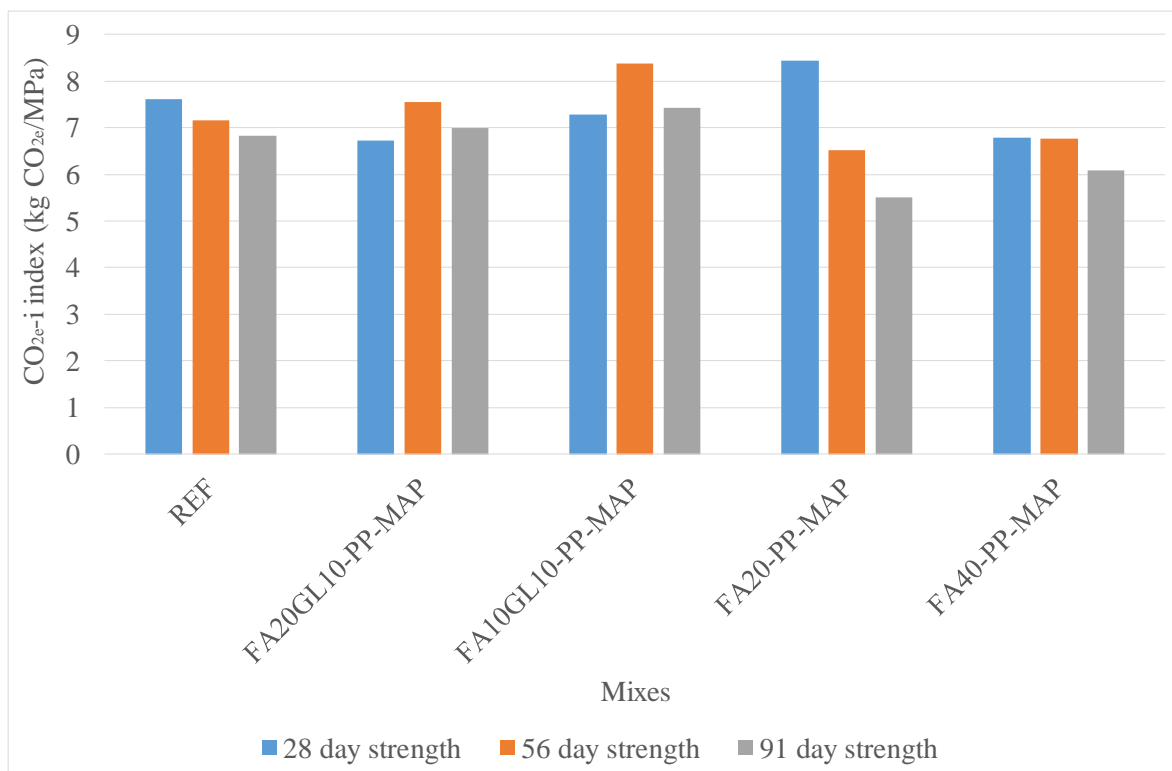
Figure 7.6: CO2e-i indices of optimised mixes

For both indices it can be seen that the optimised mixes show limited improvements in the efficiency of use of the cement, with regard to compressive strength. Although the cement contents, and subsequently GWPs of the mixes were drastically reduced, the negative effect this had on the compressive strength causes the indices to only show slight improvements. Due to the unusual strength development of the Mixes FA10GL10-PP-MAP and FA20GL10-PP-MAP, these mixes exhibit more efficiency at 28 days than at 56 and 91 days. Mixes FA20-PP-MAP and FA40-PP-MAP ultimately have the best indices, as the fly ash in these mixes causes strength gain until 91 days.

Nonetheless, when comparing these results with the previously established benchmarks of a binder intensity (bi) index of 13 kg binder/MPa for a 20MPa concrete at 28 days, it can be seen that these mixes, with compressive strengths ranging from 21 to 27 MPa, compare reasonably well (Damineli *et al.*, 2010). All mixes have bi indices lower than 13 kg binder/MPa, ranging from 12.81 to 9.44 kg binder/MPa, which can be seen in Table 7.3 while their compressive strengths at 28 days can be seen in Figure 7.3. It must be noted that the bi index takes into account all binders, i.e. cement and fly ash. It can be seen that especially the mixes with limestone show a good bi index, especially considering the fact that their compressive strength is very similar to the benchmark of 20 MPa. This is due to the limestone not being considered a binder due to its inertness, which causes a reduction in the bi index. It furthermore implies that replacing some fly ash by limestone, although resulting in compressive strength shortcomings, could be the more efficient solution when trying to limit the use of fly ash. This might be in cases where its eco-efficiency is not assumed to be as favourable as in this study. However, as this study assumed fly ash to be highly eco-efficient it can be said that the use of cement and binder, as well as the GWP due to the mixes, was indeed optimised in this range of mixes which were mixed under practical conditions. They compare well to the reference mixes, as well as benchmark mixes established in other studies.

Table 7.3: Bi indices of optimised mixes at 28 days

Mix	FA20-PP-MAP	FA40-PP-MAP	FA10GL10-PP-MAP	FA20GL10-PP-MAP
bi index (kg binder/MPa)	12.16	12.81	9.44	9.86

7.5 Selection of mixes with most potential

Although the optimised mixes showed a drastically reduced cement content, they had certain drawbacks, especially regarding lowered compressive strength. However, throughout this investigation other mixes were developed, also showing pronounced cement-content reductions compared to Mix REF, while maintaining compressive strength and other properties. A selection of

these mixes is discussed and compared to Mix REF and the two best performing optimised mixes, with the aid of Figure 7.7. In this figure, the bar graphs represent the CO_2e-i indices of the selected mixes. These indices have a close relationship with the cement content. The round markers, measured on a secondary axis, illustrate the compressive strengths of the mixes.
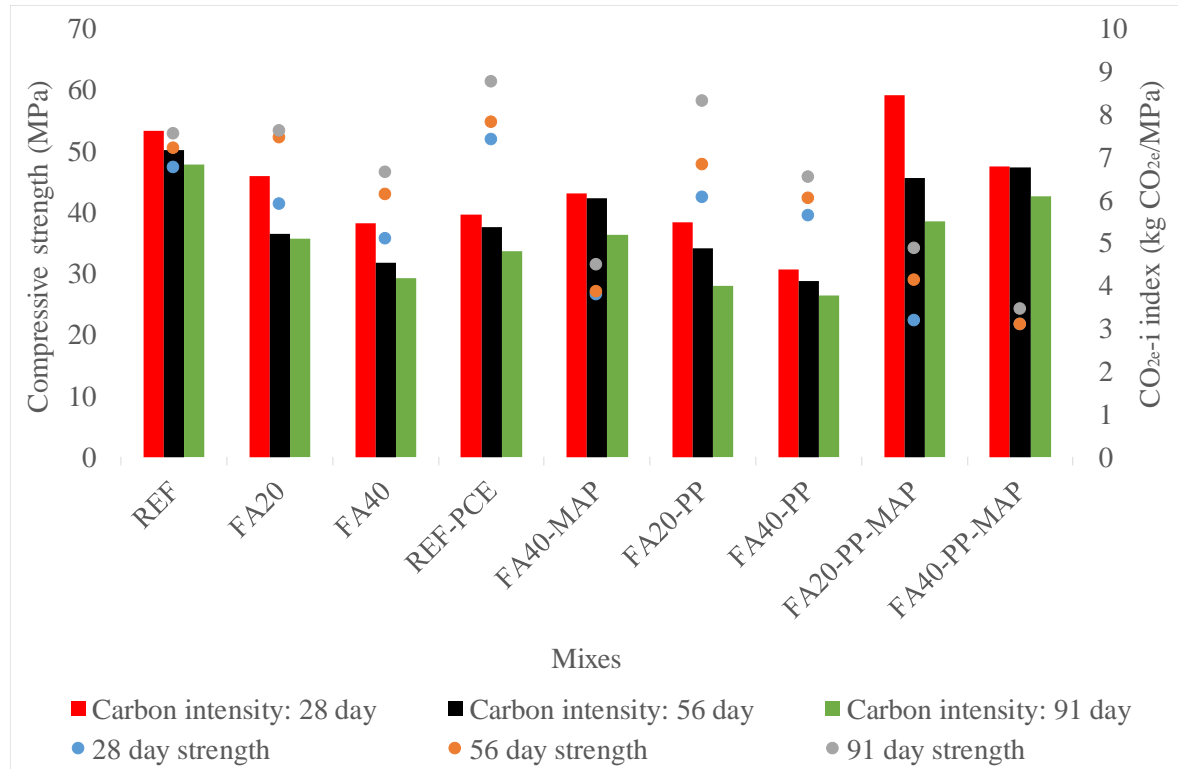
Figure 7.7: Compressive strength and CO_2e-i indices of Mix REF and selected mixes

The results show that compressive strength does not have to be sacrificed in order to achieve a more efficient use of cement and less CO_2e emissions due to a mix. They further show that although the optimised mixes have the lowest cement content and CO_2e emissions, they do not perform optimally when compressive strength, and subsequently the ci and CO_2e-i indices are considered. Nonetheless, throughout this study mixes were developed showing little compressive strength losses and a more efficient use of cement compared to Mix REF. The substitution of cement on its own shows potential in this regard, seen by mixes FA20 and FA40. These mixes show sufficient compressive strength and more efficiency than Mix REF, especially at later ages. The inclusion of superplasticisers shows decent efficiency, however challenges are seen regarding compressive strength, seen in Mix FA40-MAP. However, the approach that resulted in mixes with the most efficiency in terms of the CO_2e-i is that of optimising the particle packing of the fine aggregate. In this regard, Mix FA40-PP shows especially good results, both in terms of compressive strength and efficiency. It could thus perhaps

be described as the most optimal mix of this study, if compressive strength is considered of the same importance as the cement content as well as other properties of the mix.

To conclude, it could be said that should these mixes be applied practically, it is important that the objectives of their use are known. Should the application require less compressive strength, the optimised mixes with the lowest cement contents, GWP and adequate compressive strength could be chosen. If, however, more compressive strength is required, the most efficient mix in terms of ci and CO_{2e}-i indices can be chosen, e.g. FA40-PP.

7.6   Concluding summary

This chapter presented the optimised mixes, established by the combination of all approaches to lowering the cement content of concrete. These were found to have been significantly lowered, such that the developed mixes can indeed be termed "optimised" in this regard.

With regard to rheology, most optimised mixes showed favourable rheological properties, which can be considered an improvement to those of Mix REF. The mixes showed a slightly increased plastic viscosity, and are thus less prone to segregation, while showing less to slightly more yield stress when compared to Mix REF. The simultaneous use of superplasticisers and optimised particle packing thus showed the necessary results and produced mixes with good workability and no segregation.

The optimised mixes showed a 30% to 50% increase in setting time when compared to REF. Although this is substantial, the setting times can be considered to be within practical bounds.

The compressive strengths of the mixes were negatively influenced by the pronounced decrease in cement content of the mixes. Particularly, the early-age strengths of the mixes were affected adversely, with strengths recovering until 28 days however. After 28 days, the strength of three of the four mixes developed unusually by showing insignificant strength gains and stagnating. No reasonable explanation can be found for this behaviour. However, Mix FA20-PP-MAP showed significant strength gains until 91 days. This allows its practical use for a wide range of applications.

The optimised mixes performed well during the durability tests, showing sufficient impermeability for their OPI values to be classified as "good". This proves that there is not necessarily a need for the minimum cement content presented in most design codes to ensure durability, as the optimised mixes have around half the cement content of Mix REF.

The GWP of the mixes showed a reduction of around 50% for all mixes, with Mix FA40-PP-MAP showing the largest reduction of ca. 60%.

The ci and CO_{2e}-i indices followed the same trend due to the large contribution of cement towards the GWP. Although the cement content and GWP of the mixes had been lowered significantly, these indices were not reduced drastically, as their compressive strengths were also substantially lower than that of REF. Nonetheless, particularly at a later age both indices were improved when compared to Mix REF.

Finally, a selection of the most promising mixes established in this investigation was presented. It was shown that some of these showed more efficiency than the optimised mixes, due to maintaining compressive strength. Mix FA40-PP was pointed out as the most efficient mix in this regard. It was shown that the use of the mixes practically would therefore depend on the requirements of the application. Should lower strength be required, the optimised mixes and the lowest cement contents should be considered, while mixes showing the most efficiency and sufficient compressive strength should be considered if strength requirements are higher.

It can be concluded that although certain properties were naturally negatively affected by the drastic decrease in cement content in the optimised mixes, they nonetheless presented improvements to the Mix REF. These include the rheology, setting time, durability and GWP. Furthermore, although aspects relating to the compressive strength of the mixes were influenced negatively to a large extent, the mixes nonetheless showed strength that would permit their use in practice. Particularly at later ages up to 91 days, Mix FA20-PP-MAP showed sufficient strength. This also again showcases the need for the design of concrete according to specific performance requirements, e.g. for strength at 91 days if that is required. If this were to be applied on a wider scale, the optimised mixes presented here, and developed under very practical conditions, might well be ready for use in practice.

The next chapter provides the final conclusions and recommendations for this study.

Chapter 8

Conclusion and Recommendations

This chapter presents the conclusion of the investigation into reducing the embodied carbon content of concrete by reducing its cement content. Conclusions are provided for each approach and on the combination of these, before recommendations for future work are given.

8.1 Conclusions

The aim of this research was to significantly lower the Greenhouse Warming Potential (GWP) of a conventional concrete mix, by drastically lowering its cement content. This was to take place at a constant slump and water/binder ratio, while not sacrificing certain plastic and hardened properties of the concrete. Three approaches were implemented, namely the replacement of cement by fly ash and limestone, and the reduction of the concrete's water requirement by superplasticisers or optimised particle packing, resulting in a lower binder content at a constant water/binder ratio.

The following conclusions can be drawn from the approach of replacing cement by fly ash and ground limestone:

- At a constant slump, the replacement of cement resulted in increased dynamic yield stress and similar plastic viscosity in mixes with sufficient R^2 values. This is contrary to the popular assumption that fly ash mostly increases consistency (i.e. lowers yield stress) when replacing cement and could impact practical mix designs. However, the rheological results generally need to be interpreted carefully due to the low R^2 values of most mixes.
- The known later strength gain of mixes with fly ash was observed, highlighting the need for performance driven design for project specific requirements, and not according to general requirements by industry standards or design codes. This was further illustrated by the cement intensity (ci) and carbon dioxide intensity (CO_{2e}-i) indices, showing more efficiency of cement use and resultant CO_2 emissions at later ages of the concrete.
- Fly ash and limestone are efficient in reducing the GWP of a standard concrete mix, and should thus form the basis of every attempt at reducing this.

The following conclusions can be drawn from the approach involving the use of superplasticisers:

- Superplasticisers positively influenced rheological properties by slightly increasing the plastic viscosity and lowering yield stresses when added at the dosage determined by the Marsh cone. Doubling the dosage resulted in excessive viscosity.

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- The compressive strengths were lowered slightly when superplasticiser was included at the Marsh cone dosage, possibly due to lower cement contents and the exclusive interaction of superplasticiser and cement. Ci and CO_{2e}-i indices were impacted negatively as a result.
- The durability of the mixes was improved when compared to the respective reference mixes.
- The GWPs of the mixes were significantly reduced, due to prominent reductions of cement content.
- When comparing the results of tests on mixes with the Marsh cone dosage and double this dosage, the former was validated as it showed more practicality and better performance in the majority of tests.

The following conclusions can be drawn from the approach involving the optimisation of fine aggregate particle packing:

- Pronounced reductions in water requirement were noticed, possibly due to the decrease in volume of voids but possibly also due to the removal of dust from the sands. This resulted in significant reductions of cement and GWP compared to equivalent reference mixes.
- Non-excessive increases in plastic viscosity at constant yield stresses were seen, thus improving rheological properties. This could again not be completely established for some mixes due to inadequate R^2 values ($R^2 < 0.7$).
- Compressive strengths were improved when compared to equivalent reference mixes, further resulting in significant improvements of ci and CO_{2e}-i indices due to the parallel reductions of cement content and GWP.
- Durability of the mixes was improved when compared to equivalent reference mixes, as volume of voids and permeability decreased.

The following conclusions can be drawn after the combination of all approaches to develop mixes with the lowest, i.e. "optimal", cement content:

- The combination of all approaches resulted in mixes with a reduction in cement content of around 50% when compared to the reference mix.
- Rheological properties were improved by the combination of superplasticisers and optimised particle packing, as the mixes showed slight increases in plastic viscosity and limited increases in yield stress when compared to the reference mix.
- Compressive strengths were affected negatively due to the low cement contents. However, the mixes showed sufficient compressive strengths at 28 days for certain practical applications, while 91 day strengths showed further improvements.

- Durability of the mixes improved when compared to the reference mix, thus disproving the notion that a minimum cement content is needed to ensure durability and a sustainable, long service life.
- GWPs of the mixes were reduced by 45% to 60%, or around 160 to 216 kg CO_{2e}/m^3 concrete.
- C_i and CO_{2e}-i indices were influenced negatively due to lower compressive strengths. However, depending on the age of concrete, these were similar to improved when compared to the reference mix. Furthermore, mixes established throughout this study show vastly improved c_i and CO_{2e}-i indices due to maintaining high compressive strength at low cement contents. Should compressive strength and not merely low cement content be of interest, these could provide viable alternatives.
- The mixes were developed under practical conditions and are thus readily usable in practice.

8.2 Recommendations for future work

The following recommendations for future work could be considered:

- The methodology could be repeated at different water/binder ratios or slumps in order to establish a database of mixes.
- Use more/different materials in the investigation:
    - Look at different types of fly ash and ground limestone to possibly further improve properties of the concrete. Although slag is a limited resource and was thus not used, it might be worth investigating.
    - Investigate the use of more superplasticisers with better influence on compressive strength in particular.
    - Use different stone sizes and optimise their particle packing, i.e. include them in the particle packing optimisation of the mixes. This could solve the problems experienced with the rheological tests as well as further reduce the water requirement of the mixes.
- More units of functional performance should be considered in the investigation and in practice:
    - Use c_i and CO_{2e}-i in conjunction with an indicator durability in order to establish the efficiency of use of cement in terms of longevity. These indices would encompass all aspects of sustainability.
    - Put more emphasis on strength at later ages, as mixes gain significant strength after 28 days. Especially applicable for the use of concrete in practice, and the performance driven design thereof.

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Appendix A Rheology Test Results

Table A.1: Results of rheology tests

Mix	Plastic viscosity (Pa.s)	Yield stress (Pa)	mse	R²
REF	18,03	393,49	0,03	0,94
FA20	11,79	561,85	0,43	0,5
FA40	96,62	334,77	0,83	0,06
FA60	19,30	828,60	0,14	0,84
REF-PCE	104,16	245,93	0,02	0,98
FA20-PCE	59,93	440,48	0,07	0,94
FA40-PCE	21,96	615,66	0,12	0,87
REF-1.8PCE	153,60	146,97	0,03	0,95
FA20-1.4PCE	179,22	223,55	0,00	1
FA40-1.2PCE	121,46	628,53	0,07	0,87
REF-MAP	40,20	781,17	0,54	0,39
FA20-MAP	60,43	358,02	0,47	0,49
FA40-MAP	31,50	545,78	0,13	0,87
FA10GL10	48,96	590,55	0,65	0,28
FA20GL20	15,08	564,83	0,29	0,65
FA20GL10	19,22	581,56	0,06	0,93
FA30GL20	27,83	626,55	0,43	0,52
REF-PP	50,44	457,17	0,21	0,79
FA20-PP	99,80	515,95	0,79	0,11
FA40-PP	22,06	772,57	0,49	0,43
FA10GL10-PP	27,39	1170,63	0,32	0,67
FA20GL10-PP	25,01	710,03	0,38	0,55
FA20-PP-MAP	71,16	545,38	0,03	0,98
FA40-PP-MAP	27,12	551,79	0,12	0,88
FA10GL10-PP-MAP	39,12	356,80	0,10	0,89
FA20GL10-PP-MAP	15,35	567,72	0,02	0,99
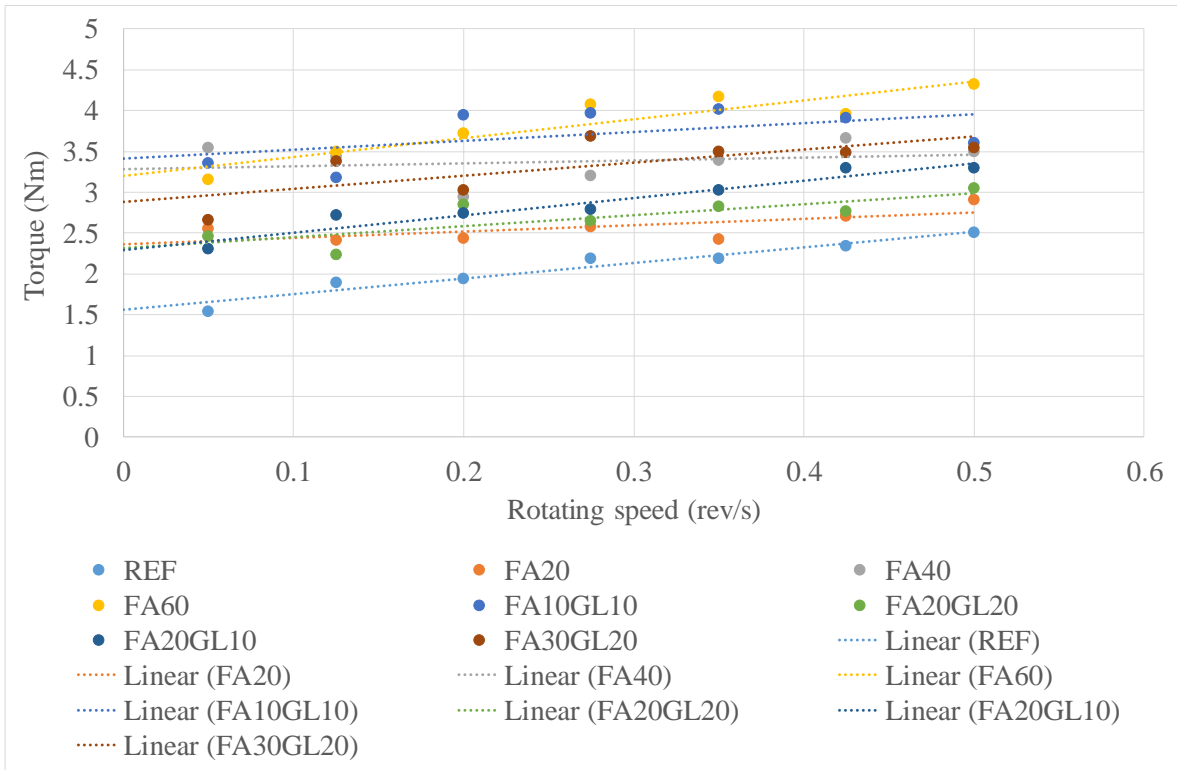
Figure A.1: Flow curve of mixes with SCM and filler
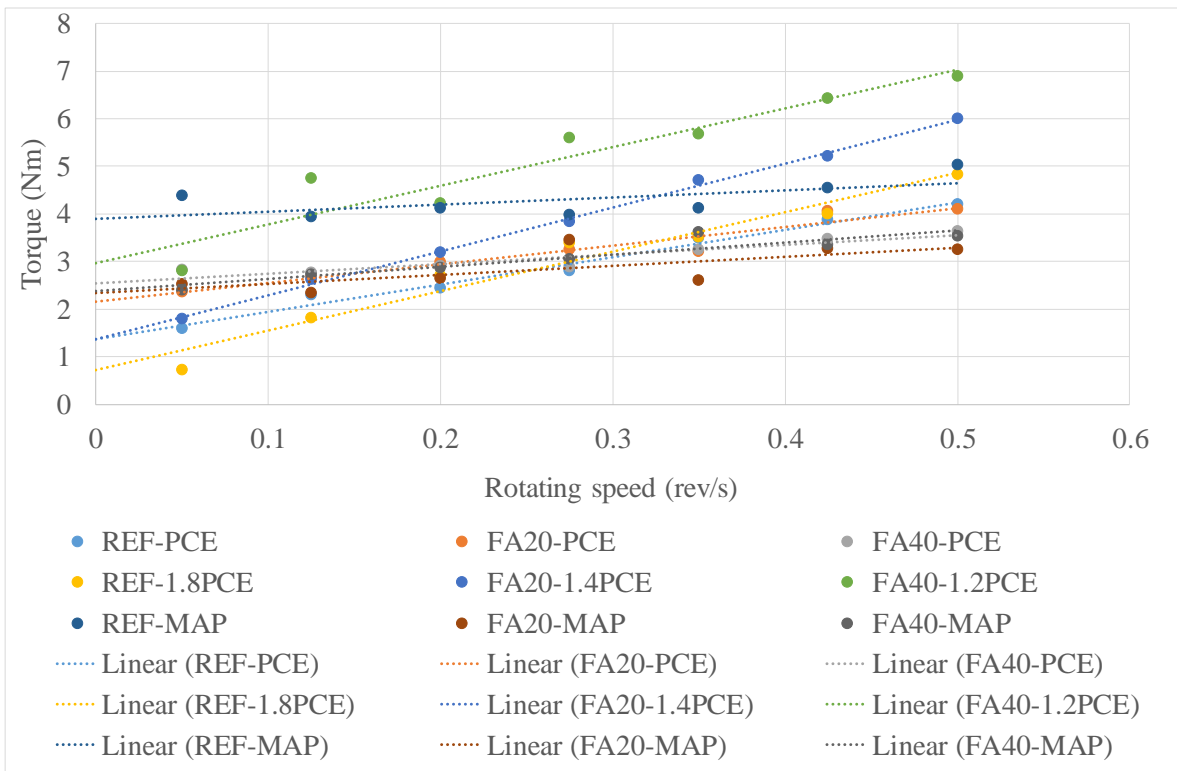
Figure A.2: Flow curve of mixes with superplasticisers

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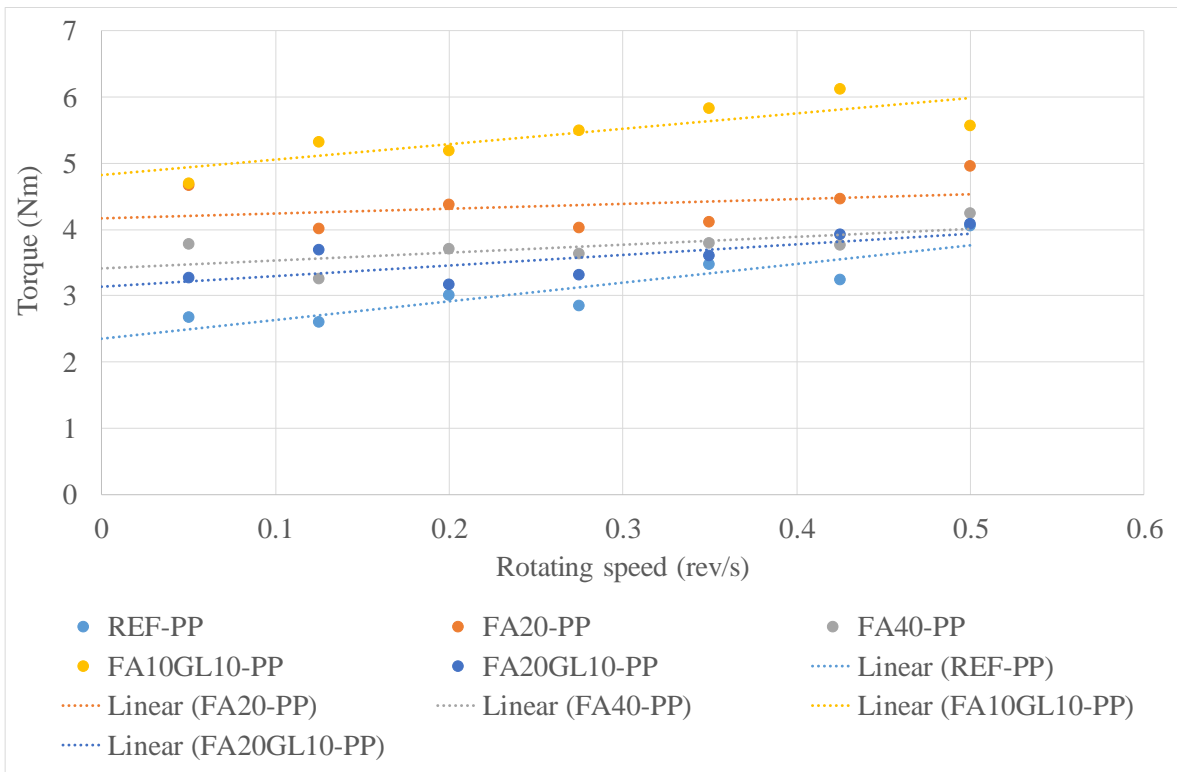
Figure A.3: Flow curves of mixes with optimised particle packing
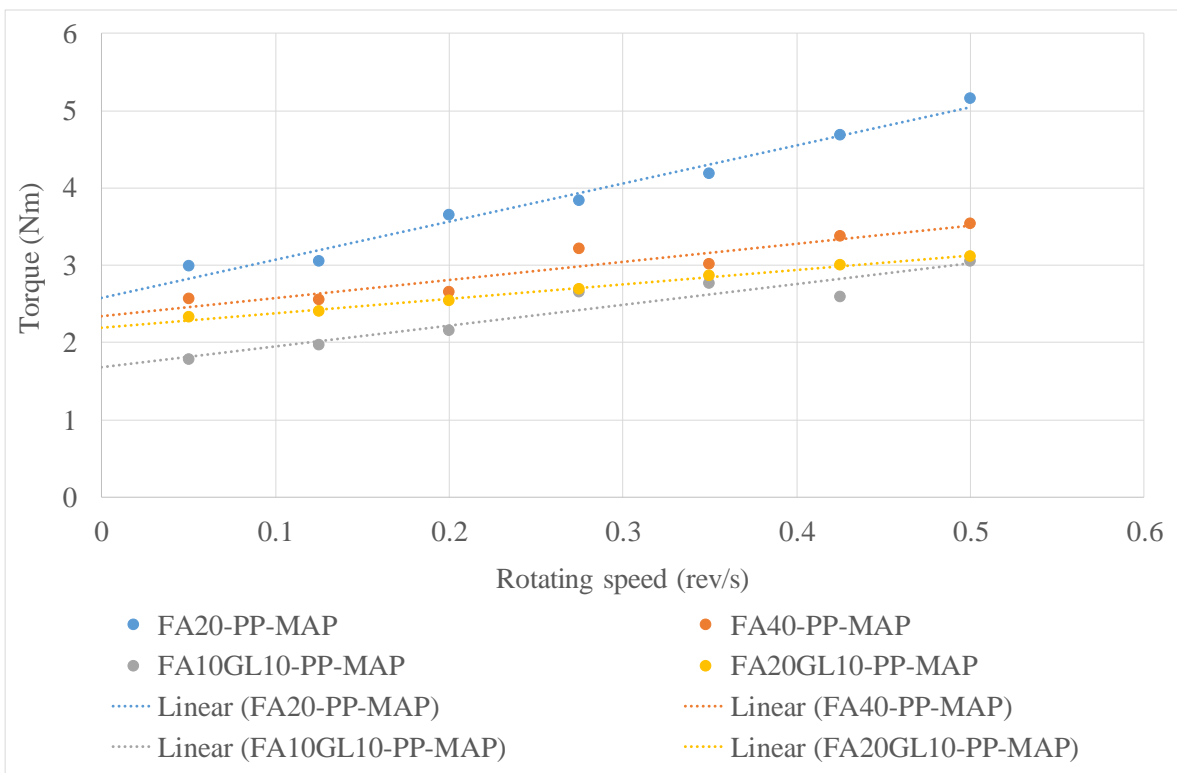
Figure A.4: Flow curves of optimised mixes

Appendix B Setting Time Test Results

Table B.1: Results of setting time tests

Mix	Setting time (min)	
	Initial	Final
REF	330	410
FA20	380	450
FA40	450	720
FA60	480	830
REF-ACC	270	380
FA20-ACC	370	450
FA40-ACC	410	610
FA60-ACC	480	730
REF-PCE	370	430
FA20-PCE	460	600
FA40-PCE	480	720
FA60-PCE	420	750
REF-1.8PCE	285	650
FA20-1.4PCE	615	790
FA40-1.2PCE	650	795
FA60-1.6PCE	680	815
REF-MAP	585	805
FA20-MAP	620	850
FA40-MAP	670	905
FA60-MAP	740	970
FA10GL10	365	520
FA20GL10	450	595
FA20GL20	400	605
FA30GL20	435	765
FA30GL30	480	820
REF-PP	270	390
FA20-PP	385	520
FA40-PP	470	770
FA10GL10-PP	360	560
FA20GL10-PP	450	605
FA20-PP-MAP	410	605
FA40-PP-MAP	505	630
FA10GL10-PP-MAP	420	550
FA20GL10-PP-MAP	450	605

Appendix C Compressive Strength Test Results

Table C.1: Compressive strength test results

Mix	Compressive strength (Mpa)					
	1 Day	3 Day	7 Day	28 Day	56 Day	91 Day
REF	14,2	36,2	42,2	47,3	50,4	52,8
FA20	9	24,2	35,1	41,3	52,1	53,2
FA40	0	15,5	22,9	35,6	42,8	46,4
FA60	0	7,8	11,8	21,2	28,3	32,8
REF-ACC	16,9	30,7	36,4	45,9	48,2	-
FA20-ACC	9,9	24,8	32	39,8	49,3	-
FA40-ACC	5,8	17	22,4	33,3	42,4	-
FA60-ACC	0	9,6	13,5	21,1	29,4	-
FA80-ACC	0	0	5,4	-	-	-
REF-PCE	11,1	27,8	35,5	51,8	54,6	61,2
FA20-PCE	5,7	17,2	21,3	30,1	32,3	39,5
FA40-PCE	0	9,2	11,6	19,2	22,1	28,4
FA60-PCE	0	0	5,7	11,2	13,4	17,4
REF-1.8PCE	19,9	39,8	46,6	57,8	62,2	63,9
FA20-1.4PCE	8,6	27,3	32,5	39,2	55	60,3
FA40-1.2PCE	0	12,8	14,3	19,6	36,5	44
FA60-1.6PCE	0	0	5,1	7,5	-	-
REF-MAP	6,1	20,9	23,1	33,5	38,0	40,5
FA20-MAP	4,3	15,9	22,3	29,5	33,5	38,3
FA40-MAP	0	9,3	16,1	26,5	26,9	31,4
FA60-MAP	0	0	5,4	9,2	-	-
FA10GL10	7,7	24,7	30,7	37,8	46,8	51,5
FA20GL20	0	12,9	20,5	28,3	34,5	38,6
FA30GL30	0	0	11,4	16,4	-	-
FA20GL10	4,9	18,5	26,9	35,3	42,7	45,4
FA30GL20	0	9	16,4	23,4	28,3	32,6
REF-PP	13,1	33,9	41,8	49,9	51,1	52
FA20-PP	7,2	28,1	37,1	42,4	47,7	58,1
FA40-PP	6,3	15,5	23,5	39,4	42,2	45,7
FA10GL10-PP	9,2	25,7	32,9	41,0	43,2	47,8
FA20GL10-PP	8,9	20,3	30,9	40,1	43,5	47,3
FA20GL10-PP-MAP	0	13,4	20,7	25,8	23,0	24,7
FA10GL10-PP-MAP	6,7	15,5	22,2	27,3	23,7	26,8
FA20-PP-MAP	5,4	16,2	21	22,2	28,8	34,1
FA40-PP-MAP	0	8,8	14,5	21,6	21,6	24

Appendix D Greenhouse Warming Potential of Mixes

Table D.1: GWP of mixes with SCM and filler

Mix		Cement	Fly ash	Ground limestone	Coarse sand	Fine sand	Stone	Total
REF	Normalised	0,976	-	-	0,005	0,005	0,015	1
	GWP (kg CO_{2e}/m^3)	351,740	-	-	1,789	1,789	5,250	360,567
FA20	Normalised	0,726	0,0004	-	0,005	0,005	0,015	0,751
	GWP (kg CO_{2e}/m^3)	261,760	0,160	-	1,888	1,888	5,250	270,947
FA40	Normalised	0,512	0,001	-	0,005	0,005	0,015	0,538
	GWP (kg CO_{2e}/m^3)	184,541	0,301	-	1,963	1,963	5,250	194,018
FA60	Normalised	0,318	0,001	-	0,006	0,006	0,015	0,345
	GWP (kg CO_{2e}/m^3)	114,520	0,420	-	2,057	2,057	5,250	124,305
FA10GL10	Normalised	0,697	0,0002	0,003	0,006	0,006	0,015	0,726
	GWP (kg CO_{2e}/m^3)	251,290	0,077	1,068	1,993	1,993	5,250	261,670
FA20GL10	Normalised	0,603	0,000	0,003	0,006	0,006	0,015	0,632
	GWP (kg CO_{2e}/m^3)	217,588	0,152	1,056	1,986	1,986	5,250	228,018
FA20GL20	Normalised	0,517	0,0004	0,006	0,005	0,005	0,015	0,549
	GWP (kg CO_{2e}/m^3)	186,504	0,152	2,113	1,973	1,973	5,250	197,964
FA30GL20	Normalised	0,420	0,001	0,006	0,006	0,006	0,015	0,452
	GWP (kg CO_{2e}/m^3)	151,330	0,222	2,057	2,000	2,000	5,250	162,860
FA30GL30	Normalised	0,327	0,001	0,008	0,006	0,006	0,015	0,362
	GWP (kg CO_{2e}/m^3)	117,792	0,216	3,002	2,045	2,045	5,250	130,350

Table D.2: GWP of mixes with superplasticisers

Mix		Cement	Fly ash	Coarse sand	Fine sand	Stone	Superplasticiser	Total
REF-PCE	Normalised	0,785	0	0,006	0,006	0,015	0,002	0,814
	GWP (kg CO_{2e}/m^3)	283,028	0	2,239	2,239	5,250	0,685	293,441
FA20-PCE	Normalised	0,581	0,0004	0,006	0,006	0,015	0,001	0,610
	GWP (kg CO_{2e}/m^3)	209,408	0,128	2,329	2,329	5,250	0,493	219,938
FA40-PCE	Normalised	0,408	0,001	0,007	0,007	0,015	0,001	0,438
	GWP (kg CO_{2e}/m^3)	147,240	0,240	2,394	2,394	5,250	0,396	157,914
FA60-PCE	Normalised	0,250	0,001	0,007	0,007	0,015	0,001	0,281
	GWP (kg CO_{2e}/m^3)	90,307	0,331	2,488	2,488	5,250	0,486	101,350
REF-MAP	Normalised	0,690	-	0,007	0,007	0,015	0,002	0,720
	GWP (kg CO_{2e}/m^3)	248,672	0,000	2,464	2,464	5,250	0,669	259,519
FA20-MAP	Normalised	0,588	0,0004	0,006	0,006	0,015	0,001	0,617
	GWP (kg CO_{2e}/m^3)	212,026	0,130	2,307	2,307	5,250	0,428	222,448
FA40-MAP	Normalised	0,422	0,001	0,006	0,006	0,015	0,001	0,451
	GWP (kg CO_{2e}/m^3)	152,148	0,248	2,337	2,337	5,250	0,341	162,662
FA60-MAP	Normalised	0,270	0,001	0,007	0,007	0,015	0,001	0,300
	GWP (kg CO_{2e}/m^3)	97,506	0,358	2,360	2,360	5,250	0,393	108,226
REF-1.8PCE	Normalised	0,740	-	0,007	0,007	0,015	0,004	0,771
	GWP (kg CO_{2e}/m^3)	266,668	-	2,346	2,346	5,250	1,291	277,901
FA20-1.4PCE	Normalised	0,552	0,0003	0,007	0,007	0,015	0,003	0,583
	GWP (kg CO_{2e}/m^3)	198,938	0,122	2,418	2,418	5,250	0,936	210,081
FA40-1.2PCE	Normalised	0,395	0,001	0,007	0,007	0,015	0,002	0,426
	GWP (kg CO_{2e}/m^3)	142,332	0,232	2,451	2,451	5,250	0,766	153,481
FA60-1.6PCE	Normalised	0,236	0,001	0,007	0,007	0,015	0,003	0,268
	GWP (kg CO_{2e}/m^3)	85,072	0,312	2,581	2,581	5,250	0,915	96,711

Table D.3: GWP of mixes with optimised fine aggregate particle packing

Mix		Cement	Fly ash	Ground limestone	Coarse sand	Fine sand	Stone	Total
REF-PP	Normalised	0,826	-	-	0,006	0,006	0,015	0,852
	GWP (kg CO_{2e}/m^3)	297,752	-	-	2,142	2,142	5,250	307,287
FA20-PP	Normalised	0,617	0,0004	-	0,006	0,006	0,015	0,644
	GWP (kg CO_{2e}/m^3)	222,496	0,136	-	2,219	2,219	5,250	232,320
FA40-PP	Normalised	0,452	0,001	-	0,006	0,006	0,015	0,479
	GWP (kg CO_{2e}/m^3)	162,946	0,266	-	2,213	2,213	5,250	172,887
FA10GL10-PP	Normalised	0,618	0,0002	0,003	0,006	0,006	0,015	0,647
	GWP (kg CO_{2e}/m^3)	222,728	0,068	0,946	2,232	2,232	5,250	233,456
FA20GL10-PP	Normalised	0,550	0,0004	0,003	0,006	0,006	0,015	0,580
	GWP (kg CO_{2e}/m^3)	198,438	0,139	0,963	2,171	2,171	5,250	209,133

Table D.4: GWP of optimised mixes

Mix		Cement	Fly ash	Ground limestone	Sand	Stone	Super-plasticiser	Total
FA20-PP-MAP	Normalised	0,490	0,000	-	0,014	0,015	0,001	0,520
	GWP (kg CO_{2e}/m^3)	176,688	0,108	-	5,210	5,250	0,356	187,613
FA40-PP-MAP	Normalised	0,376	0,001	-	0,014	0,015	0,001	0,406
	GWP (kg CO_{2e}/m^3)	135,461	0,221	-	5,060	5,250	0,304	146,295
FA10GL10-PP-MAP	Normalised	0,520	0,000	0,002	0,014	0,015	0,001	0,552
	GWP (kg CO_{2e}/m^3)	187,578	0,057	0,797	5,051	5,250	0,379	199,112
FA20GL10-PP-MAP	Normalised	0,448	0,000	0,002	0,014	0,015	0,001	0,481
	GWP (kg CO_{2e}/m^3)	161,685	0,113	0,785	5,055	5,250	0,373	173,261