

# **Interaction between clinker, calcium sulphate and superplasticisers in cement-based mixes**

by  
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## Declaration

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## ABSTRACT

Modern cement contains an increasing number of extenders, resulting in a variation in the composition of the cement, while the use of chemical admixtures is also becoming a normal addition to a modern concrete mix. These additions, when used in combination with each other, often result in unpredictable or even undesired concrete behaviour, better known as concrete incompatibilities. Superplasticisers, in particular, are known to be one of the most common admixtures to be associated with these incompatibilities. A complex interaction exists between these additions and the cement, especially the clinker phases thereof, in a concrete mix, and while the mechanism of superplasticisers is relatively well known, it is still not clear as to why these incompatibilities occur. Research suggests that the positively charged  $C_3A$  component of cement influences the absorption of the superplasticiser in a concrete mix, instead of reacting exclusively with the sulphate found in the concrete mix, as when no superplasticiser is added. While no definite statement can, however, be made as to why these compatibility issues between cement and superplasticisers occur, the reaction between calcium sulphate,  $C_3A$  and superplasticiser is believed to be the most likely justification and is therefore looked into.

This study investigates the effect of added bassanite ( $CaSO_4 \cdot 0.5H_2O$ ) and gypsum ( $CaSO_4 \cdot 2H_2O$ ) respectively when used in combination with different types and dosages of superplasticisers in an attempt to identify incompatibilities that may arise due to the combination of these additions, while also varying the clinker components, especially the  $C_3A$  percentage. The objective of this study is purely to identify compatibility issues as well as the combination of factors leading up to these incompatibilities, in an attempt to understand the reaction between superplasticisers and cement, which can then be further investigated to eventually be able to eliminate undesired concrete behaviours.

The results show that the addition of both the gypsum as well as the bassanite, decreases the flowability of the paste, as the dosage increase. On the other hand, Polycarboxylic Ether (PCE) superplasticisers increase the flowability of the mixture, proportionally to the dosage of the superplasticiser, with the Naphthalene based superplasticiser, being less effective than the PCE superplasticisers. As specified by the manufacturer, CHRYSO Optima 206, a PCE based superplasticiser (SP2), is more compatible with cements manufactured in the Western Cape, which in this study is Clinker 2. CHRYSO Optima 203, a PCE based superplasticiser (SP3), is specified to be compatible with low alkali cements, which is also confirmed by the results of this study.

Various effects on the strength gain, setting times and flowability occurred when considering the different combinations of additions to the reference mixes, with possible compatibility issues being the cause thereof. The use of the clinker containing the medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content was found to result in more compatibility issues than that of the other two clinkers considered, while the high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content clinker was found to be associated with slightly less concrete incompatibilities. The high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  content clinker showed hardly any incompatibilities when used in combination with calcium sulphate and superplasticisers. This study only aimed to identify these inconsistent behaviours and incompatibilities as a basis for further research, needed to confirm the chemical reaction responsible for these occurrences.



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# 1. INTRODUCTION

## 1.1. Background information

Concrete is known to be one of the most successful building materials and consists of a mixture of cement, water, sand and stone. With a high characteristic strength as well as the ability to be easily moulded into nearly any shape, concrete can be considered the most widely used construction material (Biggs et al., 2010). The production and processing of cement and cement-based materials, used in concrete, is however associated with 8.0% of the CO<sub>2</sub> emissions worldwide (Andrew, 2018).

With the popularity of concrete as a building material and the high production emission thereof, with a global average of 866kg CO<sub>2</sub> per tonne of clinker produced (WBCSD, 2006), more sustainable variants of the original high-clinker cement have been introduced. Clinker is made by heating limestone and clay or shale in a kiln at a very high temperature of around 1500°C. The clinker is then ground fine in a mill together with a source of sulphate, most commonly gypsum, to produce ordinary Portland cement, known as OPC (Hewlett, 2003).

Mineral additions or extenders are further added to either the OPC as a cement extender during the production process, or directly during the mixing process. These extenders are not only used to lower the carbon footprint of the production process of cement, by lowering the percentage clinker in cement but can also aid in lowering the costs of concrete and improving specific properties thereof (Biggs et al., 2010). In addition, the production of OPC is also continuously changing and depends on the raw materials (limestone, clay and gypsum) used, the burning process and agents, the cooling process as well as the milling process and grinding agents used. For example, several cement production plants started to use waste automotive tyres as an additional fuel source for heating the kilns used for cement production.

Together with the increasing use of extenders in cement, various admixtures are also incorporated in concrete mixes to create more environmentally friendly mixes. The use of water-reducing agents, superplasticisers, in particular, are gaining widespread acceptance around the world. With the need for more environmentally friendly building materials becoming a necessity, cement producers are continuously changing and optimising the production process by, for example, incorporating new technologies in the production process and/or increasing the number of extenders added to the clinker. Although these changes do not generally negatively influence conventional concrete mixes, it does, however, affect how admixtures react with the cement.

In South Africa, but also globally, where the cement production process is continuously changing, it becomes necessary to be able to predict the interaction between the OPC, admixtures and extenders

in the concrete mix. Issues that often occur result from several factors which include; the chemical proportions of the OPC and extended cement, the particle size of constituents used in the concrete mix, the amount and type of admixture added as well as the time of addition and the mixing time thereof (Burgos-Montes et al., 2012).

The complex interaction between these admixtures, extenders and OPC in concrete mixtures can sometimes lead to the unpredictable and undesirable performance of concrete known as concrete incompatibilities. These include issues such as rapid loss of workability and flowability as well as fast setting times and inadequate strength gain. These issues often occur unexpectedly in concrete which has been used successfully for some time, due to slight changes in the cement and/or admixture composition during production. One of the most common admixtures which are prone to these concrete incompatibilities is superplasticisers (Biggs et al, 2010).

Gypsum can be considered as a fundamental cement extender, primarily added to clinker in order to regulate the setting time of cement. Gypsum is known to react with the  $C_3A$  component of cement, forming ettringite, which delays the setting of concrete (Frigione, 1983).  $C_3A$  is considered to be the most reactive phase found in clinker, while also having the greatest attraction towards superplasticisers (Alonso and Puertas, 2015) and is therefore suspected to govern incompatibilities when considering the use of superplasticiser in concrete mixes.

As a result, this study focuses on the interaction between the different clinker phases, calcium sulphate and superplasticisers as a starting point to determine the cause of incompatibility issues when considering the use of superplasticisers in concrete mixtures.

## 1.2. Significance and motivation

The interaction between admixtures and cement can lead to undesired effects in a concrete mix. Together with the increased use of these admixtures and the varying constituents of cement, it becomes increasingly difficult to predict the interaction between these different components and the influence of the interaction on the performance of the concrete. Currently, there is still a lack of understanding regarding these interactions between Portland cement clinker, calcium sulphates and admixtures, particularly superplasticisers, and the associated undesired effects, known as incompatibilities (Jadhav, 2016).

The improved understanding and prediction of the interactions between cement clinker, calcium sulphate and superplasticisers will not only aid in producing concrete mixes of a higher quality but can also reduce the occurrence of concrete incompatibilities. This, in turn, will save costs for both the

construction industry as well as the cement manufacturer as less concrete will be wasted and concrete structures of increased quality and longer lifespan will be erected.

### 1.3. Objective of study

This study aims to determine the interaction between different superplasticisers and Portland cement clinker with and without added gypsum and bassanite (calcium sulphates) respectively to identify compatibility issues between these constituents.

To observe and test compatibility issues are complex, and no standard test setup or method exists. This study aims to observe and identify issues using standard flowability, setting and strength tests, to determine whether these relatively simple tests can be used to identify compatibility issues without the need for more complex chemical and rheology tests. This study can, therefore, be used as a starting point into the vast problem that is incompatibilities between cement and admixtures.

### 1.4. Scope and limitations

This study focuses on producing possible incompatibilities in a cement mix by combining various dosages of superplasticiser and calcium sulphate. The circumstances in which these incompatibilities occur will then be used in order to predict the chemical interaction responsible for the undesired concrete behaviour. This research only evaluates the physical reaction between the various materials without exploring the chemistry behind the incompatibilities, serving as a starting point for further research into this topic.

A limited amount of materials available for this study restricted both the number of tests being conducted, as well as preventing the repeatability of the tests considered. A lack of information regarding the different superplasticisers considered in this study, especially the structure (side chain lengths in particular) of the Polycarboxylic Ether (PCE) type superplasticiser, limits the depth into which the interactions leading to the concrete incompatibilities can be analysed.

### 1.5. Brief chapter overview

In Chapter 2 a theoretical background is given on concrete and its constituents, cement and the composition thereof as well as chemical admixtures, focussing primarily on water-reducing agents. Previous research in this field is also investigated in this chapter.

The experimental framework is given in Chapter 3 and discussed in terms of the objectives thereof, the materials used and the mix design, the testing methods and procedures, as well as the testing program.

In Chapter 4 and 5, the results of the various tests are analysed, discussed and compared in an attempt to identify possible compatibility issues.

The conclusions are drawn in Chapter 6.

Scanning electron microscope (SEM) images of the materials used in this study can be found in Appendix A, while Appendix B contains the Energy-dispersive X-ray spectroscopy (EDS) analysis results, visually representing the chemical composition of the various materials. In Appendix C1, the particle size distribution of the different material used in this study can be seen, with the formulas used to calculate the bassanite/gypsum additions, summarised in Appendix C2. In Appendix D, all of the results obtained during this study can be found.

## 2. LITERATURE REVIEW

This chapter contains definitions of concrete related aspects, and more specifically cement, focussing on understanding the chemical, as well as the physical properties thereof. Gypsum, mineral additions or extenders and the role they play in cement are discussed as well as modern admixtures, with special attention to water-reducing agents, and the effect on concrete mixtures. Finally, previous research in this field is also discussed.

### 2.1. Concrete

Concrete is made up of three basic components which include water, aggregate (either fine in the form of sand or coarse in the form of stone) and Portland cement. In this mixture the cement and water react with each other and harden through a chemical reaction referred to as the process of hydration, binding with the aggregates which are considered to be non-reactive in the process. In addition to the constituents mentioned, other materials can also be included in the concrete mix. Small quantities of chemical admixtures can be included to alter the behaviour of the concrete, or fine powders in the form of binder additions, replacing a percentage of the Portland cement but also taking part in the hydration process.

Concrete is one of the oldest and most versatile building materials in the construction industry. The materials required to produce concrete are easily available and can be transported to be mixed on-site, making it possible to use in most locations.

Concrete has high compressive strength and can be used in conjunction with other construction materials, such as steel to achieve higher tensile strength, also known as reinforced concrete (Ingham, 2013). The concrete mix can be altered to suit a specific application, the workability thereof, the strength as well as the setting times can be adjusted by varying the ratio of the constituents in the concrete mix. Due to this, together with the ability of concrete to be cast in different shapes, concrete is considered to be the most widely used manufactured material in terms of volume (Biggs, et al., 2010).

Two of the three components that make up a concrete mix, namely water and aggregate, are discussed in the following sections while cement is thoroughly discussed thereafter.

#### 2.1.1. Water

Water is a key component in a concrete mix, used to create a flowable paste when mixed with the dry materials. When water is combined with a cementitious material, a hard, stone-like material forms through the process of hydration (Gibbons, 2012), binding together the aggregate with the hardened cement paste to form concrete.

Water affects both the hardened as well as the fresh state of a concrete mix. In a concrete mixture, a higher water content increases the flowability of the concrete, while an overdose of water can result in segregation of the concrete. The water content, or water-cement ratio specifically, influences the hardened properties of the concrete in various ways. A lower water-binder ratio not only increases the strength of the concrete, but it can also aid in lowering the permeability (Aïtcin and Flatt, 2016), and in turn increases the water-tightness of the concrete, due to the increased density associated with the low water-cement ratio.

### 2.1.2. Aggregates

Aggregates make up for the bulk of the concrete mix as it is used to occupy most of the volume. Different types of aggregate can be used; including sand, natural gravel and crushed stone or crusher dust. The aggregate is nearly always considered to be stronger than the binder when considering conventional concrete (Mindess et al., 2003) and would thus not have a negative influence on the strength of the mixture.

The grading of the aggregate play an important role on the concrete mix, as a poorly graded aggregate will leave an increased amount of voids compared to that of a well-graded aggregate, which would require an increase in the amount of cement paste to fill the voids (Quiroga and Fowler, 2003). The same is true for angular aggregates, as the use thereof increases the number of voids in a concrete mix compared to aggregates with a smooth surface.

The particle size of the aggregate, as well as the distribution (grading) thereof also play an important role in the amount of water required by a concrete mix to be both workable and flowable in the fresh state. A mix containing aggregate with a finer particle size requires more water to have the same workability than a mix with a coarser aggregate, as there is a bigger surface area to cover with water (Yally et al., 2018). The shape of the particle can also influence the water demand of the concrete. A particle with a rounder, more spherical shape requires less water to achieve the same flowability than an angular particle. This is primarily due to the ability of the spherical particles to effortlessly move over each other, with a decrease in friction forces compared to the rough-edged particles.

### 2.1.3. Cement

Cement is a binder material that reacts with the water in a concrete mixture to harden and bind together the other materials in the concrete through the process of hydration.

In general, Portland cement is the most common type of cement used and is the most important ingredient of concrete, mortar and many plasters. It consists of a mixture of calcium silicates, aluminates and ferrites. These ferrites combine calcium, silicon, aluminium and iron in forms which



react with water. Clinker is made by heating limestone - a source of calcium, with clay or shale - a source of silicon, aluminium and iron, in a kiln at a very high temperature. The clinker is then ground fine in a mill together with a source of sulphate, most commonly gypsum, to produce Portland cement (Hewlett, 2003).

Supplementary cementitious materials, also referred to as cement additions or extenders are often added to the Portland cement as an extender as discussed in Section 1.3. These materials increase the volume of the cement delivered, with the same amount of clinker, resulting in a more economically and environmentally friendly alternative. These materials can also be used as a substitution for cement in certain concrete mixes, allowing for more sustainable use of cement (Samad et al., 2017).

## 2.2. Composition of cement

Portland cement clinker is defined as a hydraulic material which, by mass, consists of at least two-thirds calcium silicates;  $(\text{CaO})_3\text{SiO}_2$  and  $(\text{CaO})_2\text{SiO}_2$ . The remainder of the mass is made up of a combination of aluminium oxide ( $\text{Al}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ) and other oxides (Hewlett, 2003).

Portland cement clinker is made by milling raw materials into a fine powder which is then burnt in a kiln at temperatures of 1450-1500°C using coal as a heat source.

Mix design is used to determine the proportions of the different materials in the raw meal. This mix design is based on the required parameters needed to achieve specific clinker compositions, these parameters include the lime saturation factor (LSF), silica ratio (SR) and aluminium modulus (AM). The chemical composition of the raw materials used in the production process also affects the proportions required (Quality Assurance Manager; PPC De Hoek, 2019, personal communication).

The raw materials used in the production of Portland cement clinker includes:

- Limestone, a source of calcium ( $\text{CaO}$ )
- Corrective materials such as sand, a source of silica ( $\text{SiO}_2$ )
- Clay or shale, a source of alumina ( $\text{Al}_2\text{O}_3$ )
- Iron source, for example, iron ore ( $\text{Fe}_2\text{O}_3$ )

These materials are homogenized and milled into a fine powder called raw meal. This raw meal is fed into the kiln where it is burnt, reaching temperatures of up to 1500°C where clinker minerals are formed (Winter, 2009). The four main clinker minerals formed in the kiln are (Zhang et al., 2011):

- Tricalcium Silicate ( $\text{C}_3\text{S}$ ), also referred to as Alite
- Dicalcium Silicate ( $\text{C}_2\text{S}$ ), also referred to as Belite
- Tricalcium Aluminate ( $\text{C}_3\text{A}$ ), the aluminate phase

- Tetracalcium Aluminoferrite ( $C_4AF$ ), the ferrite phase

Rapid cooling is used to cool the clinker. Thereafter the clinker is milled, together with small quantities of gypsum to control the setting time of the cement, to form Portland cement (Winter, 2009). Figure 2.1 shows a pictorial representation of a typical cement grain, highlighting the different minerals as mentioned, as well as MgO (magnesium oxide) and CaO (calcium oxide) typically found in cement.

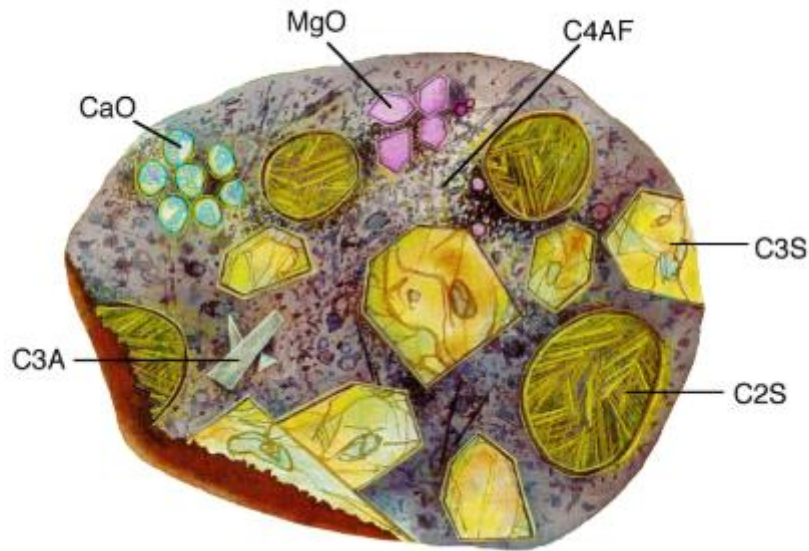


Figure 2.1: Representation of a typical cement grain, including the different minerals (Cnx.org, 2019)

### 2.3. Cement types

Additions or extenders are typically added either as a supplement or a replacement to cement in a concrete mix to achieve or enhance certain properties and is discussed in further detail in Section 2.6. Since most of these cement additions contribute to the hydration process, the cement and SCM, as defined earlier, is referred to as a binder, with the water-binder ratio being used instead of the more familiar water-cement ratio.

These additions can either be added to the concrete mix as a separate material or it can be pre-blended into cement. Various types of cement are produced by incorporating different types and/or quantities of additions, resulting in different concrete properties suitable for different types of applications. The five main types of cement, as specified by SANS 50197-1 (2013), are briefly discussed as follows. The exact quantities and types of additions added in each blended Portland cement can however still vary, resulting in a larger number of speciality types of cement (Biggs et al., 2010).

- CEM I is a Portland cement containing at least 95% ground clinker with the additional 5% made up of other minor additional constituents, which includes the addition of gypsum.
- CEM II is known as a Portland composite cement containing Portland cement with an addition of up to 35% of any other single constituent or a with up to 35% of a mixture of these constituents, which include; micro silica, limestone powder, either a natural or calcined pozzolan, fly ash, burnt shale and ground granulated blast-furnace slag.
- CEM III is a blast furnace cement containing Portland cement with the addition of 36-95% ground granulated blast-furnace slag.
- CEM IV is known as a pozzolanic cement and consists of Portland cement blended with 11-35% of a mixture containing any combination of the following materials; silica fume, natural or calcined pozzolan or fly ash.
- CEM V is a composite cement consisting of Portland cement blended with 25-80% of a mixture containing blast furnace slag, together with either natural or calcined pozzolan or fly ash.

## 2.4. Hydration process

The hydration process of cement takes place when water and cement react with each other to create a solid mass, binding together the constituents of the mixture. In Portland cement the following reactants play a role in the hydration process; alite, belite, aluminate, ferrite, free lime and alkali sulphates found in the clinker as well as gypsum blended and milled with the clinker. These reactants interact with each other to form four main hydration products; calcium silicate hydrate, calcium hydroxide, ettringite – the most common AFt phase and monosulphate - the most common AFm phase. (Biggs et al., 2010). Ettringite is considered to be the main AFt phase, while the balance of alumina and sulphates in the hydrated cement, as well as the availability of other ions, carbonate, in particular, influence the AFm phases present in the cement (Winter, 2009).

### 2.4.1. Main hydration products

The hydration of both the alite and the belite minerals contribute to the formation of calcium silicate hydrate gel, the alite reaction also delivers a substantial amount of calcium hydroxide while only a slight amount of the calcium hydroxide is produced by the belite reaction. The hydration of aluminate, in the presence of sufficient sulphate, as well the ferrite hydration reaction produces ettringite, together with other phases (Winter, 2009).

#### 2.4.1.1. Calcium silicate hydrate

Calcium silicate hydrate is a gel, or can also be described as an amorphous or poorly crystalline form of calcium silicate hydrate, that forms during the hydration reaction of the alite- and belite components and can make up between 50% and 60% of the hardened cement paste (Shah, et al.,

1995) This hydration product is shortened to C-S-H in cement chemistry notation, as well as for use in this study. The dashes in the notation indicate that no particular ratio of the C, S and H components are implied as the ratio of calcium to silica typically varies in Portland cement.

Alite ( $C_3S$ ), as seen in the scanning electron microscope (SEM) images in Figure 2.2 and 2.3, has a calcium silica ratio typically of about 3:1. The hydration of alite, therefore, results in an excess of calcium after the formation of the calcium silicate hydrate component. This excess calcium oxide again reacts with water to form calcium hydroxide. The hydration reaction of alite can be expressed in chemical notation:  $2C_3S + 6H \rightarrow C_3S_2 \cdot 3H + 3CH$  (Biggs et al., 2010).

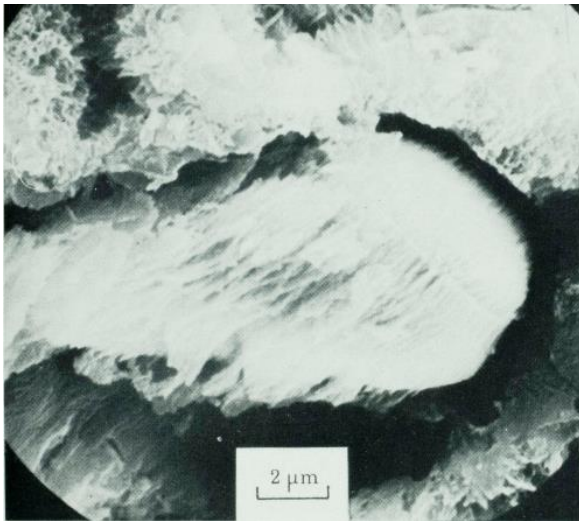


Figure 2.2: SEM image of  $C_3S$  core. (Pratt et al., 1983)

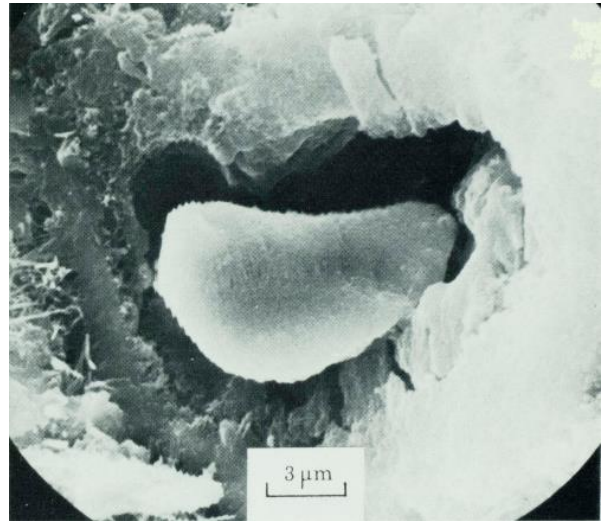


Figure 2.3: SEM image of  $C_3S$  core. (Pratt et al., 1983)

Figure 2.4 and 2.5 show SEM images of belite ( $C_2S$ ), which has an approximate calcium to silica ratio of 2:1. This means that after the formation of calcium silicate hydrate as the primary product of the belite hydration reaction, little to no calcium or silica remains to produce other hydration products. Generally, a small amount of calcium hydroxide is likely to form as a secondary product of the belite hydration reaction. The hydration reaction of belite can be expressed as  $2C_2S + 4H \rightarrow C_3S_2 \cdot 3H + 3CH$  (Biggs, et al., 2010).

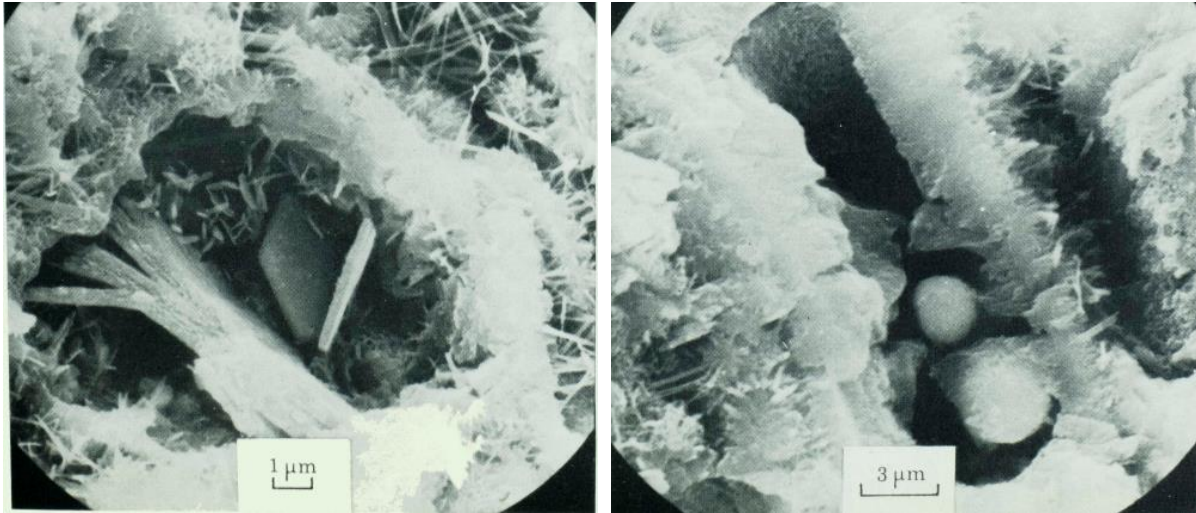


Figure 2.4: SEM image of C<sub>2</sub>S core. (Pratt et al., 1983)

Figure 2.5: SEM of C<sub>2</sub>S emerging in C<sub>3</sub>S core. (Pratt et al., 1983)

It is typically advantageous to maximise the proportion of calcium silicate hydrate produced during the hydration reaction as it is considered to be the main contributor to strength gain in hydrated Portland cement (Hedges, 2017).

#### 2.4.1.2. Calcium hydroxide

As mentioned, calcium hydroxide (CH) is primarily produced during the hydration reaction of alite, while also forming during the hydration of the free lime present in the cement (Winter, 2009). CH makes up for about 20-25% of the hardened cement paste (Shah, et al., 1995). Calcium hydroxide also affects the strength of the cement paste. During a process called carbonation, the calcium hydroxide reacts with the carbon dioxide in the air to form calcium carbonate. This carbonation is favourable as it increases the mechanical strength of the concrete. However, carbonation is also responsible for the decrease in pH of the concrete, which increases the risk of corrosion of the reinforcement rebar in the concrete, as the passivated surface of the rebar dissolves at pH levels below 10 (Panesar, 2019).

#### 2.4.1.3. Ettringite

When cement is first introduced to water, the aluminate phase reacts with dissolved calcium sulphate to form ettringite, which has the chemical formula of  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ . Ettringite crystals, seen in the SEM images in Figure 2.6 and 2.7, which makes up between 10 and 15% of the hardened cement paste (Shah, et al., 1995), form an insoluble layer which coats the surface of the hydrating crystals of the aluminate phase, providing a barrier to prevent the aluminate phase from violently reacting with water, retarding the hydration process thereof. Ettringite is usually formed for up to 1-2 days after reacting with water (Winter, 2009).



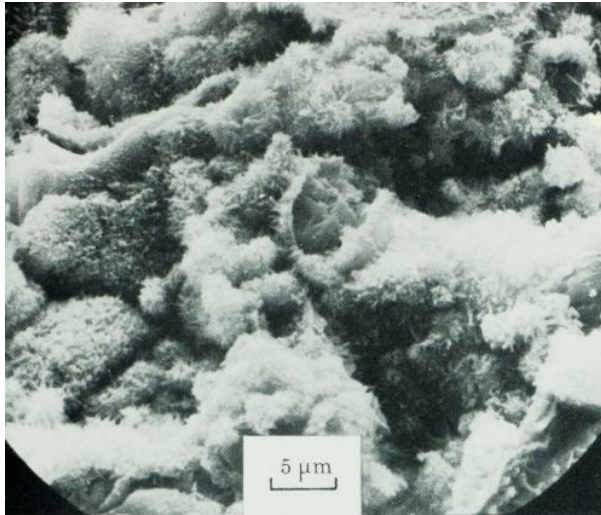


Figure 2.6: SEM image of ettringite rods. (Pratt et al., 1983)

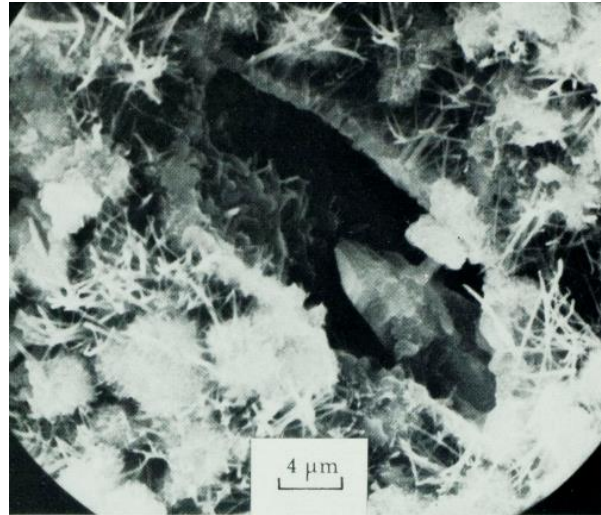


Figure 2.7: SEM of coarse Aft fibres. (Pratt et al., 1983)

#### 2.4.1.4. Monosulphate phase

The calcium monosulphate hydrate, abbreviated to monosulphate, has the chemical formula of  $\text{Ca}_4\text{Al}_2\text{O}_6(\text{SO}_4)\cdot 14\text{H}_2\text{O}$ . Monosulphate tends to only form at a later stage in the concrete mix, generally one to three days after being mixed with water. Monosulphate is similar to ettringite as it is also a hydrated compound containing calcium, aluminium and sulphate, however, the proportions of these compounds differ, as seen from the chemical notation (Winter, 2009).

During the early stages of the cement hydration reaction, most of the clinker sulphate and the gypsum is available to react, while the majority of the aluminate phase is contained within the cement particles and prevented from reacting with water. As the reactions continue, the supply of gypsum and clinker sulphate in the mixture becomes exhausted. This decrease in the ratio of available sulphate to aluminate results in the formation of monosulphate instead of ettringite.

Sulphates present in cement are either added to the clinker during the milling phase or are found in the clinker itself, known as clinker sulphates. The type of clinker sulphate found in cement is determined by the ratio of clinker alkali to that of the sulphates, while the type of alkali also plays a role. Some of the main forms of clinker alkali sulphates include; arcanite ( $\text{K}_2\text{SO}_4$ ), calcium langbeinite ( $\text{K}_2\text{SO}_4\cdot 2\text{CaSO}_4$ ), while clinkers with a higher Na/K ratio are likely to contain aphthitalite ( $3\text{K}_2\text{O}\cdot \text{Na}_2\text{O}\cdot 4\text{SO}_3$ ), clinkers with a high level Na and a low level K, may contain thenardite ( $\text{Na}_2\text{SO}_4$ ) while clinkers with high sulphates and low alkalis are likely to contain anhydrite ( $\text{CaSO}_4$ ) (Winter, 2009)

### 2.4.2. Heat of hydration

An exothermic reaction occurs during the hydration process of cement. The rate at which heat is emitted varies for approximately three days, after which it gradually declines. The general shape of the evolution of heat during this reaction is plotted in Figure 2.8.

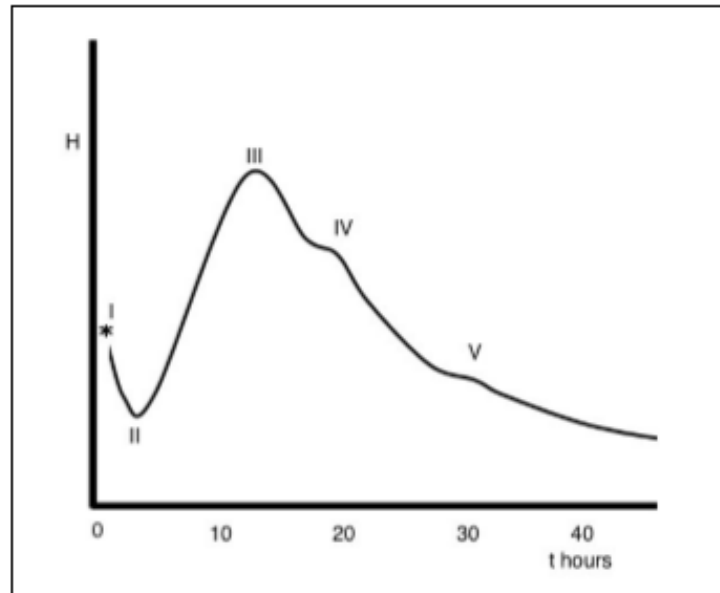


Figure 2.8: Evolution of heat during hydration of cement. (Winter, 2009)

The initial reaction, with a high rate of heat evolution, lasts only for a couple of minutes and is primarily due to the hydration reactions of the aluminate and alite phases, as well as the hydration of calcium sulphate hemihydrate to the dihydrate form. This initial reaction is then followed by a dormant period in which the rate of hydration slows down. This period, before the concrete sets and where the concrete paste is workable, is due to the very early products forming a layer on the surface of the cement particles, acting as a barrier to restrict further reactions (Biggs et al., 2010). This layer is eventually broken down at which the dormant period of the cement paste ends.

The rate of alite and aluminate hydration starts to increase again, this together with the belite component also starting to hydrate, increases the heat evolution again at Point III in Figure 2.8, After this, the small increases in heat evolution can be linked to both the hydration of ferrite as well as the formation of ettringite (Winter, 2009).

The rate of heat evolution gradually decreases as the amount of unhydrated cement particles becomes less, with those that remain being surrounded by a dense hydration product that hinders any possible further reaction.

### 2.4.3. Setting and hardening

The result of the hydration process of cement is a hard, stone-like material. During the hydration process, both setting and hardening are considered to describe the physical changes of the paste, however, these two terms have different meanings.

Setting refers to the transition of the cement paste from being in a flowable, liquid state to a hard, rigid state. Initial- and final set are used as arbitrary definitions to determine the setting characteristics of a cement paste. Hardening, on the other hand, refers to the increase in strength of a concrete mix. This rate of strength gain, or rate of hardening, is independent to that of the setting of a cement paste.

For the normal setting of concrete, it is usually considered to take between 4 and 8 hours for the paste to set, with the full strength for design purposes typically recognised at 28 days, while at only 7 days, the concrete would be expected to have reached at least 70% of its 28-day strength. Flash setting can, however, occur if an insufficient amount of sulphates are found in the concrete mix. Sulphates, both from the added gypsum as well as the clinker sulphates, play an important part in slowing down the hydration reaction of  $C_3A$ . When an insufficient amount of these sulphates are available to decrease this reaction, rapid hydration of the  $C_3A$  produces AFm phase (monosulphate phase) in the form of hydroxy-AFm (Winter, 2009). These crystals form a link between the different particles in the concrete mix, causing a rapid hardening of the paste. This increase in the hydration of the  $C_3A$  results in an increase in the heat generated during the reaction, while the strength of the concrete declines due to the flash setting.

On the other hand, if an excess of sulphates is found in a concrete mix, usually in the form of hemihydrate, false set is likely to occur. The hemihydrate dissolves in water to then reprecipitate as gypsum in the mix, which again results in a rapid setting of the concrete due to a link forming between the different particles. However, because the  $C_3A$  hydration is inhibited by the sulphate, no rapid heat generation occurs as with the flash setting. False set can be reversed, unlike flash set, by continuing to mix the concrete paste, the gypsum crystals linking together the particles in the mix can be broken, after which the remaining gypsum fragments will dissolve and normal setting of the concrete can occur with the strength gain thereof being fairly normal compared to regular setting of concrete (Winter, 2009).

The contribution of the hydration of each component to that of the hydration reaction of cement can be seen in Figure 2.9, showing how the hydration products increase over time.



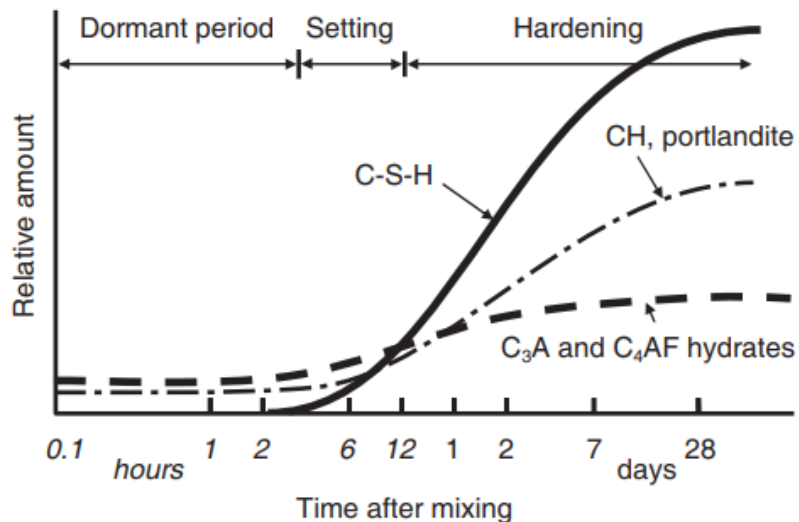


Figure 2.9: Formation of hydration products over time. (Domone and Illston, 2001)

## 2.5. Gypsum

Gypsum is an important component of cement and is mainly used for regulating the setting time thereof. Without the addition of gypsum, cement clinker can react immediately when it is mixed with water causing flash set to occur. The C<sub>3</sub>A component in the clinker can quickly dissolve in water to generate a calcium aluminate hydrate, which acts as a clotting agent, causing the cement to set. The retardation mechanism of gypsum can be explained as follows: when cement is hydrated, gypsum reacts with C<sub>3</sub>A to generate calcium sulpho-aluminate hydrate, also referred to as ettringite, as seen in the reaction:  $C_3A + 3\text{C}\hat{\text{S}}\cdot 2\text{H} + 26\text{H} \rightarrow C_3A\cdot 3\text{C}\hat{\text{S}}\cdot 32\text{H}$ . This forms a coating on the cement particles to hinder the hydration of C<sub>3</sub>A causing a delay in the setting time of the cement (Frigione, 1983). The appropriate amount of gypsum needs to be added to the clinker during the production process of cement. When not enough is added, the retardation effects are not noticeable while too much gypsum accelerates the setting time of cement, as gypsum can generate a clotting agent itself. The amount of gypsum should account for around 3-5% of the cement's mass.

Although gypsum is mainly used to control the setting time of cement, too high content of gypsum could lower the strength of concrete (Wright et al., 2016).

## 2.6. Cement additions

Additions, which can also be referred to as supplementary cementing materials, mineral- additives or admixtures, fillers, cement replacement or substitutes, latent hydraulic materials and cement extenders, are defined according to BS EN 206 (2000) as finely ground materials used in concrete to either improve the properties thereof or to add special properties to the concrete mix (BS EN 206, 2000).

These additions are typically inorganic materials used to either replace a portion of the cement in the concrete mix or as an addition, supplementing the cement in the concrete (Biggs et al., 2010). Additions are fine material with a particle size similar to or smaller than that of cement. The use of additions in cement is not only used to enhance the concrete properties, but it is also financially and environmentally beneficial.

Different types of materials can be used as additions in cement, some of which are obtained as by-products from other industrial processes, which not only provides both environmental and sustainability benefits but also creates a potential for economic advantages (Biggs et al., 2010). Additions, in summary, not only aids in improving concrete properties but also lowers costs associated with the production of cement and recycling waste.

The extent to which a cement addition is active during the hydration process relates to the effect the addition has on the hardened properties of the cement paste and varies from one type of addition to another. Cement additions can be classified into two types of inorganic additions, as recognised by BS-EN 206 (2000), based on the contribution of the addition during the hydration reaction as discussed in the following sections (BS EN 206, 2000).

#### 2.6.1. Type 1: Nearly inert additions

Type 1 additions are materials that are not hydraulic and cannot produce a pozzolanic reaction and include materials such as; ground limestone, ground quartz sand, slow cooling slag and various other kinds of waste slag (Biggs et al., 2010). Although these additions are unable to produce a chemical reaction with water or even the other components in the cement mixture, some increase in the rate of strength gain can be related to the addition of these inert materials, by improving the particle packing of the paste, as well as acting as a nucleus for the reaction of the cement hydration products. Some reactions were also found to occur between the calcium carbonate, found in the ground limestone addition, with the aluminate phases present in the cement, again contributing to the rate of strength gain (Domone and Illston, 2001).

#### 2.6.2. Type 2: Pozzolanic or latent hydraulic additions

The additions in this category, referred to as pozzolanic materials, contain active silica. These materials are not cementitious but chemically reacts with calcium hydroxide when exposed to moisture, to form cementitious compounds in the form of calcium silica hydrates (Domone and Illston, 2001). When these pozzolanic materials are used in combination with ordinary Portland cement, the silica reacts with the calcium hydroxide product formed during the hydration of the silicates in the cement. It is noted that the silica reaction is dependent on the product formed during the hydration reaction of the cement, these Type 2 additions are therefore also referred to as latent hydraulic materials.

The reaction of these pozzolanic additions can be described by the chemical formula:  $S + CH + H \rightarrow C-S-H$ , with the active silica ( $SiO_2$ ) component abbreviated as S and the calcium hydroxide as CH (Biggs et al., 2010). The three most commonly used pozzolanic additions are fly ash, slag and silica fumes as discussed in the following sections.

#### 2.6.2.1. Fly ash

Fly ash is a by-product of coal-fired electric generating plants; the ash from pulverised coal, used as fuel for the power stations, are collected from the outlet gases before it is discharged into the atmosphere (Domone and Illston, 2001). The properties of fly ash depend on the type of coal burnt, therefore not all ashes are suitable for use in concrete due to various factors such as the composition and particle size. Fly ash produced in South Africa contains a small percentage of CaO – less than 10% (Beushausen et al., 2013) and is therefore classified as siliceous ash. In general, siliceous fly ash is pozzolanic as it does not react with water, but reacts with water in the presence of lime or cement (Winter, 2009), while calcareous fly ash has latent hydraulic properties as it is only slightly reactive in water with an increased reactivity when activated by an alkaline material in the presence of water, such as lime or cement.

Fly ash has a particle size similar to, or smaller, than Portland cement. Fly ash particles have a spherical shape, which can either improve the fluidity of a concrete paste if no other alterations are made to the mix design, or it can be used to decrease the water demand of a concrete mix due to enhanced workability associated with the particle shape of the fly ash. This can result in a lower water binder ratio and therefore an increase in the strength development of the hardened paste.

#### 2.6.2.2. Ground granulated blast-furnace slag

Ground granulated blast-furnace slag, also referred to as GGBS, is by-product of steel production and is formed when slag from the “scum” that is formed during the smelting of iron in a blast furnace, is quenched in water and is then ground to achieve a particle size similar to that of Portland cement (Domone and Illston, 2001). GGBS has latent hydraulic properties due to its high amount of CaO and can, therefore, be classified as a self-cementing material (U.S. Federal Highway Administration. “Ground Granulated Blast-Furnace Slag”, 2007). Two oxides; aluminium oxide and silicon oxide, make up the composition of the two active components in the blast-furnace slag (Ingham, 2013), which reacts with calcium hydroxide to achieve strength gain.

#### 2.6.2.3. Silica fumes

Condensed silica fume is a by-product of the production of silicon and ferrosilicon alloys. These extremely fine particles of silica are condensed from the waste gases emitted during the production of silicon metal (Domone and Illston, 2001). Silica fume also referred to as micro silica, is similar to fly

ash, but has a particle size 100 times smaller. This results in a higher surface-to-volume ratio and a much faster pozzolanic reaction. Silica fume is used to increase strength and durability of concrete, but generally requires the addition of superplasticisers for workability (U.S. Federal Highway Administration. "Silica Fume", 2007).

## 2.7. Water reducing admixtures

Admixtures can either be artificial or natural materials which are added to the concrete mix besides cement, water and aggregate. These admixtures are used to improve certain properties of concrete during either the casting, setting or service stages. Admixtures can be classified into five different classes of chemical admixtures according to their function: air-entraining, retarding, accelerating, water-reducing which includes plasticisers and superplasticisers. Other varieties of admixtures are also available to be used in speciality concrete mixes, which includes a reduction in shrinkage, reduction in alkali-silica reactivity, corrosion inhibition, enhanced workability, bonding, damp proofing, and colouring (Chemical admixtures for concrete, 2010). In this study, only water-reducing agents are considered.

Water reducing admixtures are used to reduce the required water content for a concrete mixture, usually by about 5 to 10% (Hester, 1979) while maintaining a certain level of flowability. Therefore, concrete containing a water-reducing admixture needs less water to reach a required slump than a standard concrete mix. Concrete containing a water-reducing agent can thus have a lower water-cement ratio (Biggs et al., 2010) which indicates that a higher strength concrete can be produced without increasing the amount of cement added to the mix. The addition of these admixtures can also be used to contribute to a more environmentally friendly concrete mixture by decreasing the amount of cement needed in a concrete mixture to achieve a required strength, as the cement industry is known to be energy-intensive with an estimated 5-6% of all carbon dioxide greenhouse gasses generated by human activities originating from processes involved in the production of cement (Potgieter, 2012).

However, sometimes the cement content may be lowered while maintaining the original water-cement ratio to reduce costs or the heat of hydration for mass concrete pours. In some cases where the placement of concrete is challenging due to reinforcement, the nature of aggregate or even the shape of the formwork in which it is cast, water-reducing admixtures can be used solely to increase the workability of the concrete mix to aid with the placement thereof.

Water reducing agents are classified according to their water-reducing abilities, generally either as a plasticiser or superplasticiser. Plasticisers usually reduce the water demand of a mix by 5 -12%, while superplasticisers reduce the water demand by 12-30% (Biggs et al., 2010). The most commonly used

plasticiser is lignosulphonate based, which is a by-product of wood pulp. Hydrocarboxylic acids and carbohydrates are also plasticisers which are widely used. Superplasticisers can be categorized into three main groups: Polycarboxylic Ether (PCE), Sulphonated Melamine Formaldehyde (SMF) and Sulphonated Naphthalene Formaldehyde (SNF). A discussion of these plasticisers and superplasticisers follows.

#### 2.7.1. Plasticisers

Plasticisers mainly affect the fresh properties of concrete by reducing the water demand while maintaining a certain consistency. The required dosage of the water reducing agent is determined by the cementitious material (binder) content, with the increase in workability depending on both the type and the dosage of the plasticiser used.

Plasticisers can typically reduce the water demand of a concrete mix by up to 6-12% (Hester, 1979) and is required to reduce the water demand by at least 5% according to BS EN 934. Plasticisers mostly retard the setting time of a concrete mix slightly, with plasticisers that retards the setting time with more than three hours, being classified as a water-reducing admixture with retarding effects.

Two commonly used plasticisers are lignosulfonates and hydroxycarboxylic acids, with the latter requiring a higher water content than the lignosulfonate-based plasticiser. Secondary effects associated with the addition of plasticisers are common, especially at higher dosages, including a decrease in early strength gain, delayed setting time and entraining of air bubbles (Biggs et al., 2010) while increased bleeding is considered to be a common problem for concretes containing hydroxycarboxylic acids (Senft et al., 1999).

#### 2.7.2. Superplasticisers

Superplasticisers can typically reduce the water demand of a concrete mix by 12-30%, and at least 12% (Kett, 2009), while maintaining a certain level of flowability and workability, and also to achieve a lower water-binder ratio without compromising on the workability of the mix. Superplasticisers also can enhance the early strength gain of a concrete mix (Martirena et al., 2014), the reduction in the water-binder ratio due to the superplasticiser addition can significantly enhance the early strength of concrete. Unlike with the addition of plasticisers, superplasticisers do not tend to entrain air into the concrete mix although often due to the addition of detraining agents by manufacturers, there are however still disadvantages associated with the use of superplasticisers, especially rapid slump loss and a decrease in workability due to incompatibilities with the binder materials (Flatt., 2012).

Each type of superplasticiser is generally chosen for specific projects taking into account the cost thereof, its effectiveness, as well as the type of cement and cement additions it is used with.

Sulphonated naphthalene formaldehyde, for example, is the most cost-effective and commonly used for ready mixes that need to be transported over long distances while sulphonated melamine formaldehyde is preferred when doing precast concrete. Polycarboxylic ether, the most expensive of the three groups, is also the most effective and can be used to lower the water-cement ratio of a concrete mix drastically, which results in high strength concrete (Papayianni et al, 2005).

#### 2.7.2.1. Sulphonated naphthalene formaldehyde (SNF)

Sulphonated naphthalene formaldehyde is produced when petroleum or tar naphthalene is sulphonated by making use of highly concentrated sulphuric acid. This product is polymerized with formaldehyde and neutralized to the sodium or calcium salt. Figure 2.10 shows the sulphonated naphthalene repeating unit  $n$  polymer. These polymers have a relatively low molecular weight and usually repeated to form a chain of two to ten polymers, ranging in molecular weights between 500 and 2500. Better superplasticising properties are usually associated with higher molecular weight when considering the SNF based superplasticisers as the higher molecular weight fractions were found to be preferred during the adsorption of the superplasticiser (Newman and Choo, 2003).

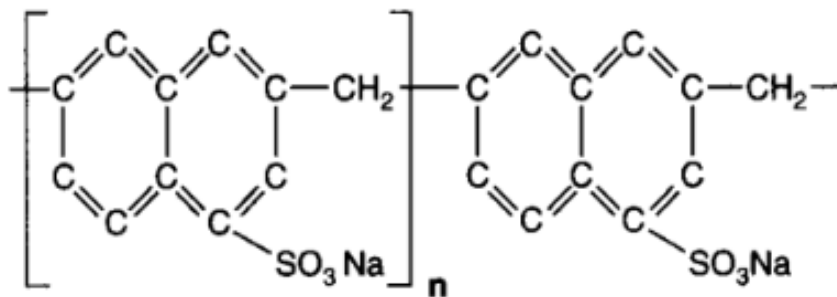


Figure 2.10: SNF repeating unit polymer (Hewlett et al., 2019)

In a solution, the  $\text{SO}_3\text{Na}$  dissociates to form  $-\text{SO}_3^-$  and  $-\text{Na}^+$ . The negative charges on the  $\text{SO}_3^-$  molecule is crucial to the adsorption of the superplasticiser onto the cement, as well as playing a key role in the mechanism of electrostatic dispersion (Newman and Choo, 2003).

#### 2.7.2.2. Sulphonated melamine formaldehyde (SMF)

The sulphonated melamine formaldehyde has a similar structure than that of the SNF. In the SMF structure, as depicted in Figure 2.11, it is noticeable that the only difference in the two structures is that a melamine ring replaces the naphthalene double ring, while the molecular weight is higher than that of the SNF molecule (Newman and Choo, 2003). The sulphonated melamine-formaldehyde polymers are only available as sodium salts, unlike that of the sulphonated naphthalene formaldehyde polymer.

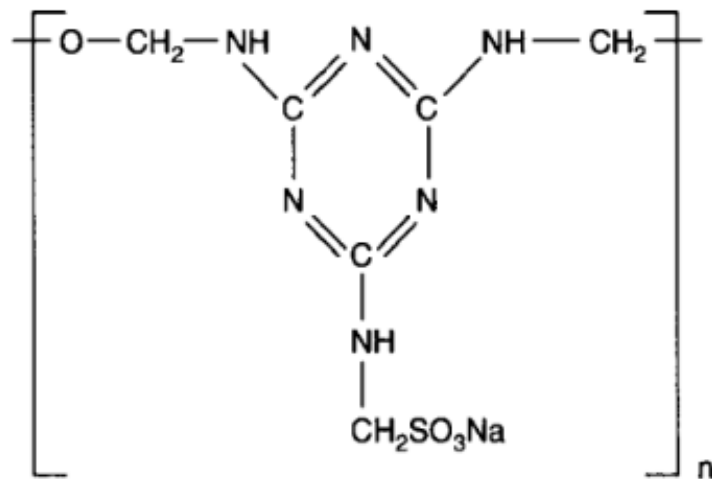


Figure 2.11: SMF polymer structure (Hewlett et al., 2019)

### 2.7.2.3. Polycarboxylate ethers (PCE)

Polycarboxylate ethers also referred to as comb polymers, are different than the SNF and SMF based superplasticiser. Both the SNF and SMF have a single structure polymer while the PCEs consist of a variety of different chemical structures. An example of a typical PCE structure is depicted in Figure 2.12.

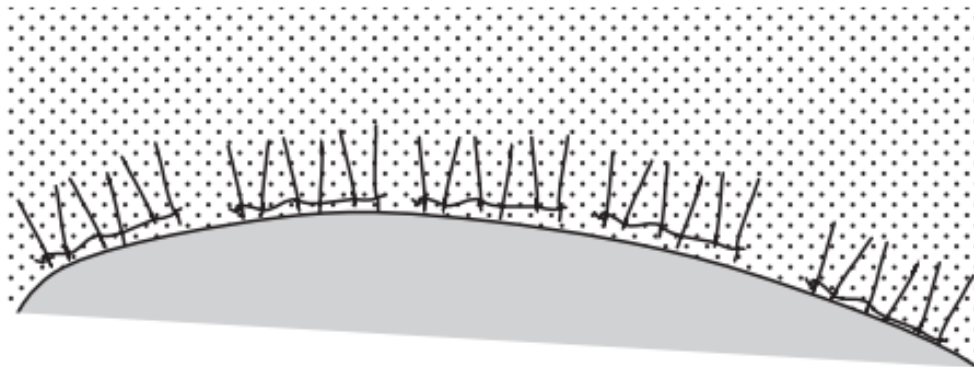


Figure 2.12: Typical PCE structure (Biggs et al., 2010).

The main or backbone polymer is generally based on the polymerization of acrylic acid but can be substituted with other monomer groups (Newman and Choo, 2003). This can also be used to modify the number of carboxylate groups along the backbone of the polymer. The carboxylate group is generally neutralized as the sodium salt and takes on a negative charge in the solution as the  $\text{-Na}^+$  dissociates and in this way provides an attachment point for the superplasticiser to adsorb onto the surface of the cement.

The copolymer is a polyether, shown as polyethylene glycol ( $\text{-CH}_2\text{-CH}_2\text{-O-}$ ) in the example structure in Figure 2.13, can vary with different types, or combinations, of polyethers. With the chain length

varying, as well as the number of polyether groups substituted along the chain and the difference in molecular weights of the various types of polyether's, a significant range of properties can be achieved. The polyether is the part of the polymer structure responsible for the dispersion of the cement particles and works by a mechanism of steric hinderance as discussed in Section 2.7.4. This basic copolymer can be changed in variable ways, making it suitable for use in specific applications, such as high early strength for concrete used in the precast industry or workability retention to be used in the ready-mix industry.

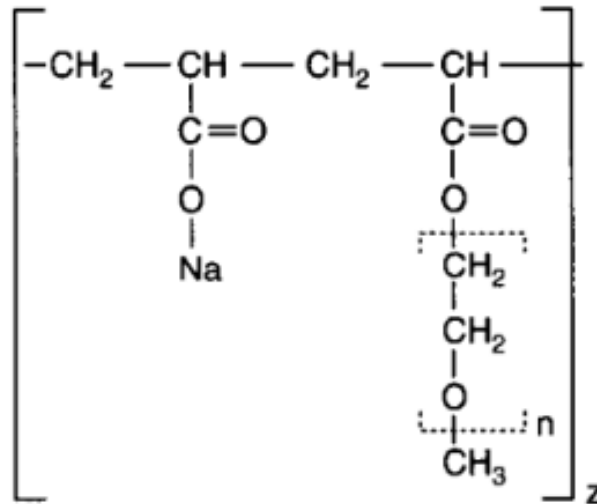


Figure 2.13: Example structure of PCE copolymer (Hewlett et al., 2010).

### 2.7.3. Adsorption versus absorption

The process of absorption refers to the process where one substance enters the body or volume of another substance. The one substance is taken by or absorbed by the other substance, usually when a liquid is dissolved by either another liquid or a solid. Absorption involves the entire surface of the absorbing substance and does not involve any forces in the process.

Adsorption refers to the process in which one substance adheres to the surface of another substance (known as the adsorbent). In the case of adsorption, intermolecular forces are involved, which attaches the molecules. Adsorption is a surfaced based process and only involves a film of the adsorbate to be created on the adsorbent. Figure 2.14 illustrates the difference between these two concepts.



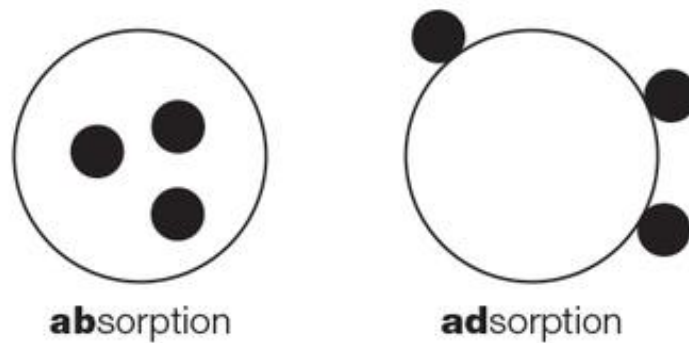


Figure 2.14: Illustration of absorption vs adsorption (<https://byjus.com/>)

#### 2.7.4. Mechanisms of water reducers

Water reducing admixtures increase the flowability of a concrete paste by dispersing the cement particles, as seen in Figure 2.15. When cement comes into contact with water, the grains tend to stick together to form small lumps, also known as flocs, instead of uniformly spreading throughout the mixture. This phenomenon is a result of the dissimilar charges at the surface of the cement particles, which attract each other to form the flocculants mentioned (Biggs et al., 2010). A big portion of the water in the mixture is trapped within these flocculants, causing the grains in the paste to be less mobile than it would have been if separated into separate grains, resulting in a less flowable and workable mixture.

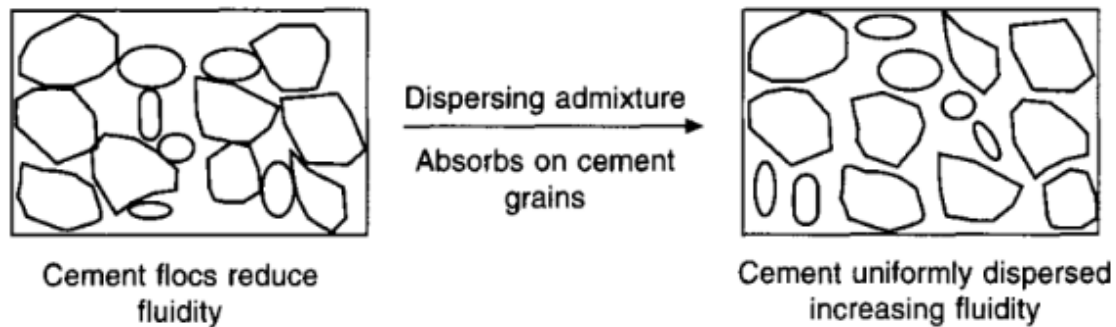


Figure 2.15: Illustration of dispersed cement particles (Newman and Choo, 2003).

Superplasticisers disperse these flocculations by adsorbing onto the surface of the cement particles and breaking up the small lumps into individual cement grains. These cement particles move more freely in the water making the mixture more flowable. This dispersive action of the superplasticiser works through one of two mechanisms namely: electrostatic dispersion and steric hindrance. Electrostatic dispersion or repulsion is the main mechanism associated with the use of SNF and SMF based superplasticisers and is illustrated in Figure 2.16.

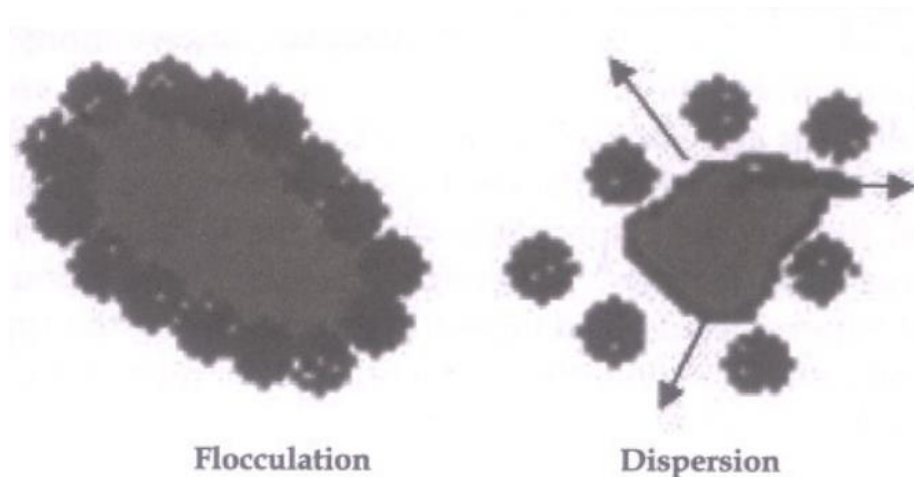


Figure 2.16: Illustration of electrostatic dispersion (Jayasree et al., 2011)

As mentioned earlier when discussing these types of superplasticisers, it was noted that the molecules of SNF and SMF based superplasticisers carry  $-SO_3Na$  groups that, when mixed with water, dissociates into  $-SO_3^-$  and  $-Na^+$  particles. The  $-SO_3^-$  particle, that stays attached to the superplasticiser, has a strong negative charge that is partly used to adsorb onto the surface of the cement grain. The remainder of this negative charge, however, orientates outward from the cement grain (Biggs et al., 2010).

Adjacent cement particles are considered to be negatively charged due to the adsorption of superplasticiser onto the particle surface and since particles with similar charges repel each other, these negatively charged cement grains, repels each other, reducing the flocculation of the cement particles, allowing for better dispersion of the grains. The adsorption of the superplasticiser can be seen illustrated in Figure 2.17, as the positively charged cement grain attracting the negative charge of the superplasticiser, the remainder of the negative charge on the surface of the cement grain is shown which in turn, repel the other cement grains, now also negatively charged due to the adsorption of superplasticiser.

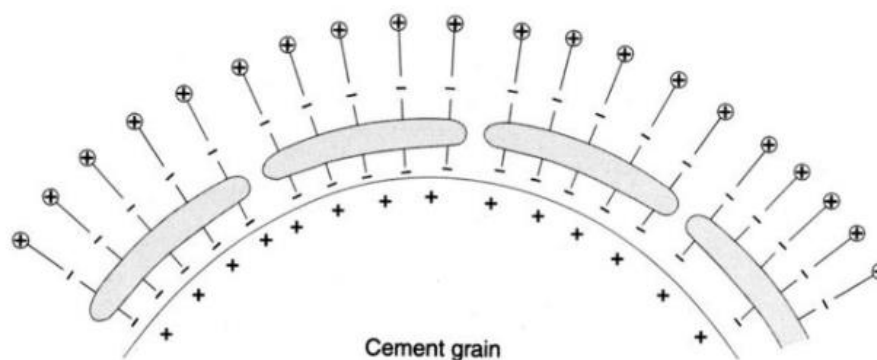


Figure 2.17: Illustration of superplasticiser adsorbed by cement grain (Hewlett et al., 2019)

This mechanism can be measured using the Zeta potential of the cement particles. The Zeta potential measurement is a measure of the charge on a particle surface. This potential was found to be positive on the surface of the cement particle before the addition of any admixtures, this charge then changed to be strongly negative with the addition, and adsorption, of superplasticiser (Newman and Choo, 2003).

Steric hindrance, as illustrated in Figure 2.12, is the primary mechanism of action for PCE based superplasticisers and is considered to be more effective than electrostatic dispersion (Biggs, et al., 2010). PCE based superplasticiser molecules carry  $-\text{CO}_2\text{Na}$  groups, that in the presence of water, disperse to form  $-\text{CO}_2^-$  and  $-\text{Na}^+$  particles. The  $-\text{CO}_2^-$  stays attached to the superplasticiser and has a moderate negative charge, that is used to attach the superplasticiser to the surface of the cement particle. The long polyether chains of the PCE admixture orientates facing away from the surface of the cement particle, as pictured in Figure 2.18. These polyether chains resist becoming entangled with polyether chains attached to adjacent cement particles and in turn, push the cement grains away from each other and increasing the flowability of the paste. Unlike with the SNF and SMF based superplasticisers, the Zeta potential measurement showed no significant negative charge on the cement particle when used in combination with PCE based superplasticisers (Newman and Choo, 2003).

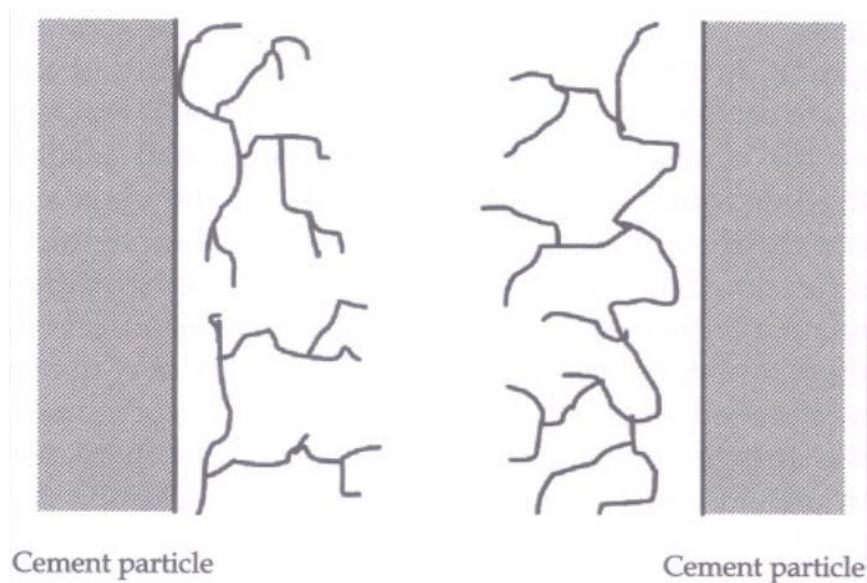


Figure 2.18: Illustration of long polyether chain of PCE (Jayasree et al., 2011).

The  $C_3S$ ,  $C_3A$ ,  $C_4AF$  and alkali components of the binder are believed to have the most significant influence on the reaction between the superplasticiser and the constituents of a concrete mix, and in turn the effectiveness of superplasticisers. As mentioned previously, the addition of gypsum in the Portland cement alters the percentages of these components and could, therefore, play an important role in the reaction between cement and superplasticiser. This is further discussed in Section 2.8.

#### 2.7.5. Compatibility issues

Water reducing admixtures such as superplasticisers and plasticisers reacts with the concrete to alter the fresh properties thereof in various ways, both chemically and physically (Bedard and Mailvaganam, 2005). Chemically, the water reducing agents can interfere with the hydration reaction of the binder in the concrete paste, while others react physically by interacting with the hydration products. This not only affects the rate of hydration but also alters the composition, as well as the morphology of the hydrated products (Sasmal and Anoop, 2019).

Compatibility issues in the context of this study refer to unfavourable effects a certain combination of cement (binder) and water reducer has on the performance outcome of a certain concrete mix. Water reducers are generally used with a specific goal in mind, however, sometimes the chemicals interact in such a way that creates an undesired effect. A few common problems associated with compatibility issues between water reduces and cement are as follows (Shrivastava et al., 2016):

- Flash setting
- Delayed setting
- Rapid slump loss
- Improper strength gain
- Segregation

These compatibility issues do not only affect the strength of the concrete but also the durability thereof. The interaction between the gypsum content in the cement and the water reducing admixture are believed to be one of the main reasons for incompatibilities when incorporating these admixtures in concrete mixes.

#### 2.7.6. Particle shape and size

One of the main factors controlling the behaviour of cement, when mixed with water, is the fineness of the cement particles (Winter, 2009). Cement ground to have a finer particle size interacts more efficiently with water than cement that is milled more coarsely, as a larger surface is available increasing the contact area exposed to the water in the mix. This also means that a finer cement particle has improved adsorption when used in combination with water-reducing admixtures. A finer particle has a smaller diameter than a coarser particle, which means that it has a higher packing

density resulting in a more viscous cement paste. As mentioned, when discussing aggregates, the smaller the particles, the higher the water demand as the exposed surface area to cover is increased.

Another aspect to take into account when considering the particle size of the binder is the grinding process of the cement. The final grinding stage in the production process of cement influences the charge on the surface of the cement particle. A longer grinding period is required to produce a cement with finer particle size, adding additional zeta charges on the cement particles. These higher charges, in turn, result in a larger attraction or repulsion force between the cement particles (Plank and Hirsch, 2007).

## 2.8. Research on compatibility issues

In this section, work conducted by other researchers relating to the compatibility between cement, gypsum and water-reducing admixtures is discussed.

Banfill (2011) attempted to demonstrate the effect of additives in cement on the rheology of fresh concrete when used in combination with water-reducing admixtures. In their study, the rheology of fresh concrete was determined as the vector sum of the effects when plotting the yield stress against plastic viscosity on a graph. Banfill (2011) used three UK type cement, either alone, in combination with 30% and 40% addition of fly ash as well as a combination of 30% fly ash and 5% silica fumes. To measure the viscosity of the concrete mix, the slump flow test method was used. Although the focus was on different binder extenders and not the calcium sulphate as in this study, the measure of flowability is still applicable as a method to determine the effects of superplasticiser on a concrete mix.

Hallal (2010) illustrated the combined effect of mineral admixtures with superplasticisers on the fluidity of the blended cement paste. In this study, a limestone cement, as well as pozzolanic cement, was tested in combination with an SNF and SMF based superplasticiser to determine the influence of these chemicals with each other. The Marsh cone test was used to determine the effect these additions have on the fluidity of the mix. It was found that the naphthalene-based superplasticiser showed an incompatibility when used in combination with cement containing a high  $C_3A$  or alkali content, such as the pozzolanic cement used in this particular case. This study claimed that the water-reducing admixture is adsorbed less on the alite and belite minerals, while it is much more adsorbed by the  $C_3A$ ,  $C_4AF$  and free  $CaO$  in the cement.

The effect of constituents on the flowability of the concrete was reviewed by Dengwu et al. (2017). In their study, the rheology of cement is classified as an effective tool used to characterise the workability, flowability and consistency of a cement paste. The effects of different cementitious

extenders, as well as a range of chemical admixtures, were investigated to determine the effect thereof on the rheology properties of the concretes. It was found that cement with a high  $C_3A$ , high alkali content, low  $SO_3$  content or a high fineness and specific surface area, has a decreased workability.

Jayasree et al. (2008) studied the flow behaviour of different types of water-reducing admixtures, at different dosages. A Lignosulphonate based plasticiser as well as SNF-, SMF- and PCE based superplasticiser were used, all at various dosages. The Marsh cone test was used to find the saturation dosage for each of the different admixtures while the mini slump test was used to determine the flow behaviour of the superplasticised cement pastes. Jayasree et al. found that, as expected, the Marsh cone flow time decreased and the mini slump flow measurement increased, as the dosage of the superplasticiser increased.

Compatibility issues of NSF-PCE superplasticiser with several different cement types as studied by Coppola et al. (2010) focussed on finding compatibility issues between different types of admixtures, especially those NSF and PCE based, and various types of cement, all available in India. Fixed workability was achieved by varying the dosages of the different admixtures. It was found that PCE based superplasticiser is generally more sensitive to the varying chemical composition of the different cement types. The SNF based superplasticiser, although more consistent in terms of its performance, was found to be less efficient in terms of water reduction than the PCE.

Valetiet al. (2017) investigated the compatibility between commercial types of cement and superplasticisers. Again, a PCE- and an SNF based superplasticiser was considered in this study, used in combination with a cement type blended with fly ash and another, blended with granulated blast furnace slag. The Marsh cone test was used to determine the workability of a mix by recording the flow time of the paste and is, according to Valeti et al. (2017) the best approach to determine the cement paste behaviour. The mini slump test, as well as compressive strength, tensile strength and flexural strength, was also considered in the study by Valeti et al. (2017). According to the findings, it was again shown that the optimal dosages of superplasticiser vary with both the type of plasticiser as well as the type of cement. It was also found that the PCE based superplasticiser is more compatible with different cement types than the SNF based superplasticiser.

Bassioni(2010) investigated the influence of cement composition on the efficiency of superplasticisers. To achieve this, four different cement types, with varying alite-, belite,  $C_3A$ - and  $C_4AF$  contents, was used in combination with an SNF- and SMF-based superplasticiser. The zeta potentials and the related adsorption of the superplasticiser on the cement particle were investigated, while the mini slump test and heat flow calorimetry were used to establish the effect these cement/superplasticiser

combinations have on the concrete mix. The cement with the low  $C_3A$  content was shown to have the best liquefying effect. The types of cement with a high sulphate and free CaO content was found to require a higher superplasticiser dosage to obtain the same workability as the other cement types. The  $C_3A$ -poor cement was found to adsorb the least amount of superplasticiser.

Some of the significant conclusion that can be drawn from these past studies are discussed as follows: As seen in Figure 2.19, according to Biggs et al. (2010), a higher dosage of the SNF based superplasticiser, of roughly 0.7%, as needed to achieve a similar flowability as when compared to that when 0.2% PCE based superplasticiser was used. According to this finding, the PCE seems to be much more effective, this is addressed in this study as both a PCE- as well as an SNF based superplasticiser is investigated.

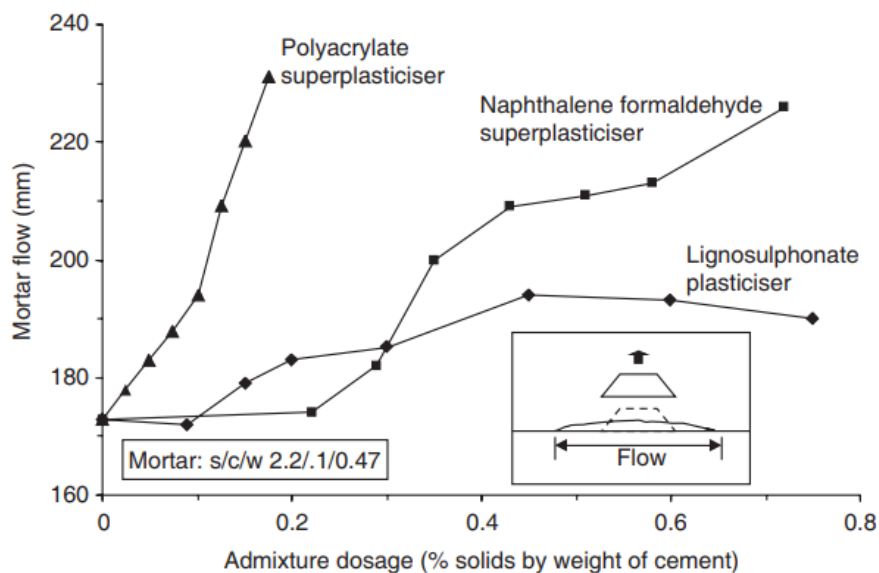


Figure 2.19: Flowability vs superplasticiser dosage for PCE, SNF and Lignosulphonate (Biggs et al., 2010)

In an effort made by Ramachandran et al. (1989) to measure slump loss of concrete containing superplasticiser, slump tests, as well as setting times and thermal analysis were done. The slump loss was thought to be related to the retarding action on the formation of ettringite from the  $C_3A$ + Gypsum reaction in some types of cement. It was found that the measured slump values of the concrete containing only the superplasticiser were lower than that of the concrete containing both superplasticisers, as well as a higher level of gypsum.

Plank and Hirsch(2007) used a method of measuring the zeta potential to determine the absorption capabilities of different materials with regards to superplasticiser. It was concluded that gypsum, with

a zeta potential of  $-0.06$  mV, has a negligible absorption rate in the early hydration phase, as a positive zeta potential is a key factor for absorption.

Yoshioka et al. (2002) concluded that the maximum absorption of superplasticiser decreased significantly in the presence of gypsum, by also using the zeta potential as a measure, backing the results obtained by Plank and Hirsch (2007). These claims with regards to the addition of gypsum are addressed later in this study as it forms a critical part of the research question.

Jayasree et al. (2011) found that the  $C_3S$  and  $C_2S$  components possess a negative zeta potential while the  $C_3A$  and  $C_4AF$  have positively charged zeta potentials. Therefore, it is believed that the preferential adsorption of the superplasticiser will be on the positively charged  $C_3A$  and  $C_4AF$  phases.

Finally, from the literature study, it was also found that both the Marsh cone- as well as the mini slump test is considered to be a popular choice when determining the workability of a concrete paste. While the  $C_3A$  component in the cement seems to be related to compatibility issues when used in combination with water-reducing admixtures.

## 2.9. Concluding summary

In this chapter concrete and its constituents are discussed while focusing on cement, the production, composition and hydration thereof. The two different classes of supplementary cementitious materials or extenders, the role it plays on cement and the effect it has on the hydration process is discussed. Thereafter, the use of chemical admixtures, specifically focussing on superplasticisers, in concrete mixes is investigated to gain an insight into the mechanism in which they work. Lastly, research previously conducted on this topic is considered, and the findings thereof discussed to give a broader insight into the problem addressed by this study. The experimental research, materials used as well as the test- design and set up are discussed in Chapter 3.



### 3. EXPERIMENTAL FRAMEWORK

In this chapter, the experimental methodology, materials, as well as the test- and mixing procedures, used in this study are discussed.

#### 3.1. Experimental methodology

This study focuses on identifying compatibility issues arising from the use of chemical water-reducing agents, particularly superplasticisers, in concrete mixes. Gypsum, found in Portland cement, plays a critical role in the hydration process of cement and, according to literature, contribute to the compatibility problems when using superplasticisers in concrete mixes.

The four tests conducted on each of the mixes in this study are chosen to identify the following compatibility issues; rapid slump loss, improper strength gain, delayed or flash setting and loss in workability. The Marsh cone test is particularly effective in understanding the flow behaviour of cement pastes containing superplasticiser and is applicable to cement pastes with a water-cement ratio beyond 0.5 (Tonitechnik, 2019) and is used in this study to determine the workability and possible loss thereof due to an incompatibility between the materials. The mini slump test, which is primarily developed to evaluate the influence of water reducing agents on cement pastes, can also be used to evaluate the loss of slump (workability) over time for various admixtures (Kantro, 1980). The mini slump test is used in this study to determine the possible loss in slump over time and is similar to the slump test done on construction sites but uses significantly less volume as well as only a cement paste or mortar and not concrete. Setting time tests are conducted to determine deviations in the time a mix takes to achieve both initial- and final set, which can then either be explained by the addition of certain materials or linked to a possible compatibility issue. Finally, the 2- and 7-day strengths of the different concrete mixes are tested to determine how the combination of different additions affects the early strength of the hardened pastes.

Figure 3.1 illustrates the sequence in which the testing procedures were conducted.

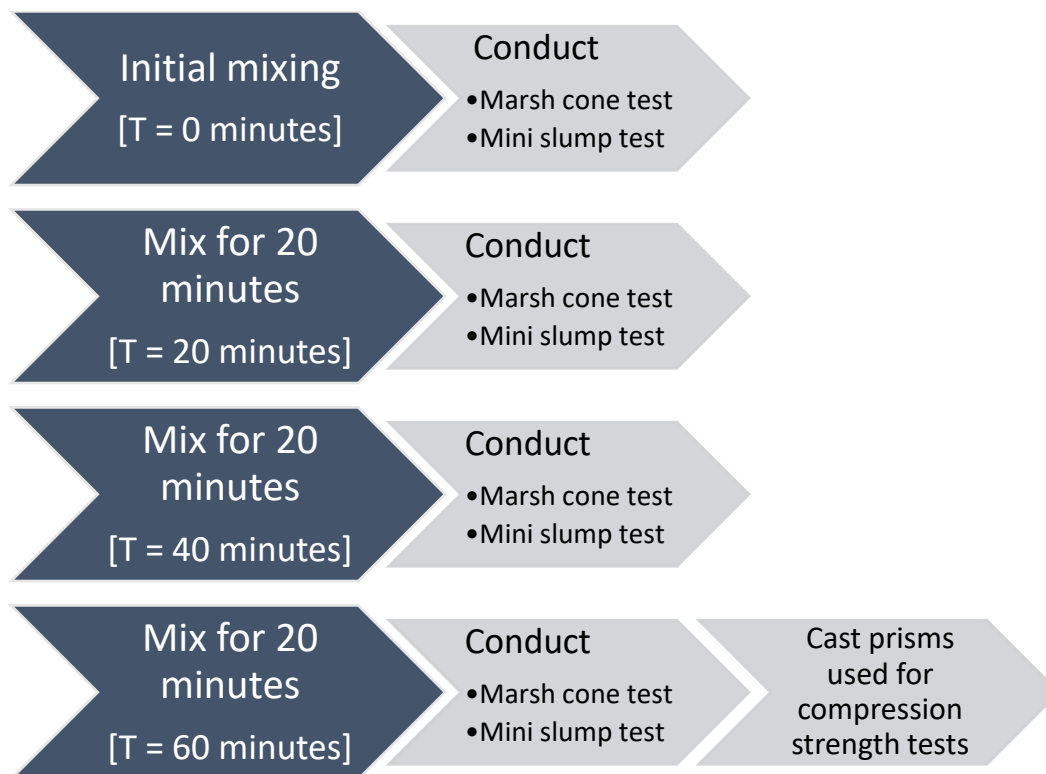


Figure 3.1: Experimental proceedings

The mixes are designed in such a way to vary in the percentages (high, medium and low) of the aluminates ( $C_3A$  and  $C_4AF$ ) and silicates ( $C_3S$  and  $C_2S$ ) components by using three different clinkers. In this study, pure clinker is used when conducting the various tests, as it does not yet contain any additions. To determine how the quantities of these components affect the effectiveness of the superplasticiser by again adding low, medium and high quantities of four different types of commonly used superplasticisers. Gypsum and bassanite are also added to the different clinkers making it possible to observe how these additions react with the aluminates as well as the silicates in the clinker. Finally, combinations of high and low dosages of both the superplasticisers and the gypsum/bassanite are tested and compared to the previously obtained results, with the aim to observe and identify any incompatibilities when combining gypsum/bassanite with chemical water-reducing admixtures.

### 3.2. Materials

To ensure a constant environment for reactions to take place in, all the materials used in this study were stored in a climate control room, where the temperature and humidity are regulated. The humidity is kept above 50% and the temperature between 22°C and 25°C. The materials were kept sealed to prevent the addition of excess moisture, while the temperature of the different materials was measured before testing to verify the temperature of 22-25°C.

### 3.2.1. Clinker

The clinker used in this study was supplied by Pretoria Portland Cement (PPC). Three clinkers, produced at different PPC plants, namely Dwaalboom, Slurry and De Hoek, was used. This was done to vary the amounts of  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  present in the clinker. The clinker was collected before the addition of any gypsum or extenders and milled using the following procedure;

- Crushed each clinker material using the Retch jaw crusher (C424).
- Screened all the clinker material using a 2 mm sieve. Sizes over 2 mm were re-crushed until it passed through the 2 mm sieves.
- All screened material was milled using the ball mill (CE 033) at 12 kg lots (capacity of the mill is 12 kg).
- Milled samples were checked for relative density and fineness.
- All milled 12 kg lots for each clinker type were finally homogenized in the Nauta mixer for 3 hours.

The clinker manufactured at the Dwaalboom factory in Gauteng had a high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content, while the clinker produced at the Slurry factory, also situated in the Gauteng region, had high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  content. The third clinker, from the PPC De Hoek factory, had a high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content. These results, together with a detailed chemical analysis can be found in Chapter 4.

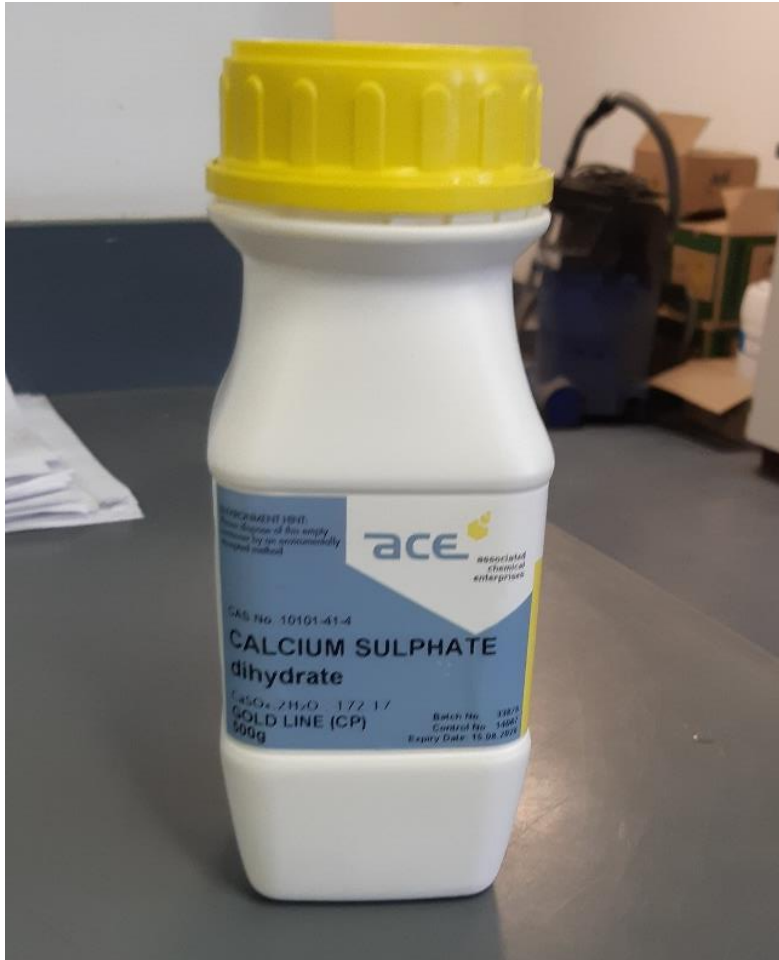
For simplification of mix names, Dwaalboom clinker is referred to as C1, De Hoek clinker as C2 and Slurry clinker as C3 throughout this document.

### 3.2.2. Bassanite

Ground bassanite was supplied by PPC for this study, in an attempt to use a calcium sulphate mineral with a similar chemical composition to that found in cement. Gypsum ( $CaSO_4 \cdot 2H_2O$ ) is a crystalline form of calcium sulphate when combined with water, is known as calcium sulphate dihydrate. When this dihydrate is dehydrated to lose 1.5 molecules of water, it transforms into calcium sulphate hemihydrate,  $CaSO_4 \cdot 0.5H_2O$ , also known as bassanite (Kilic and Kilic, 2007).

### 3.2.3. Gypsum

Gypsum, as seen in Figure 3.2, supplied by PPC and distributed by Associated Chemical Enterprises, also known as ACE, was also used in this study. Gypsum is also referred to as G2 in this document.



*Figure 3.2: ACE Gypsum used in this study*

#### 3.2.4. Sand

Sand mined from a local quarry near Goedverwacht in the Western Cape, was used in this study. The sand was dried for 24 hours and left to cool whereafter it was sieved using a 1mm sieve, before being used for testing. The grading of the sand was done by using a sieve analysis in accordance with SANS 1083 (2014). The results of this grading can be seen in Figure 3.3.

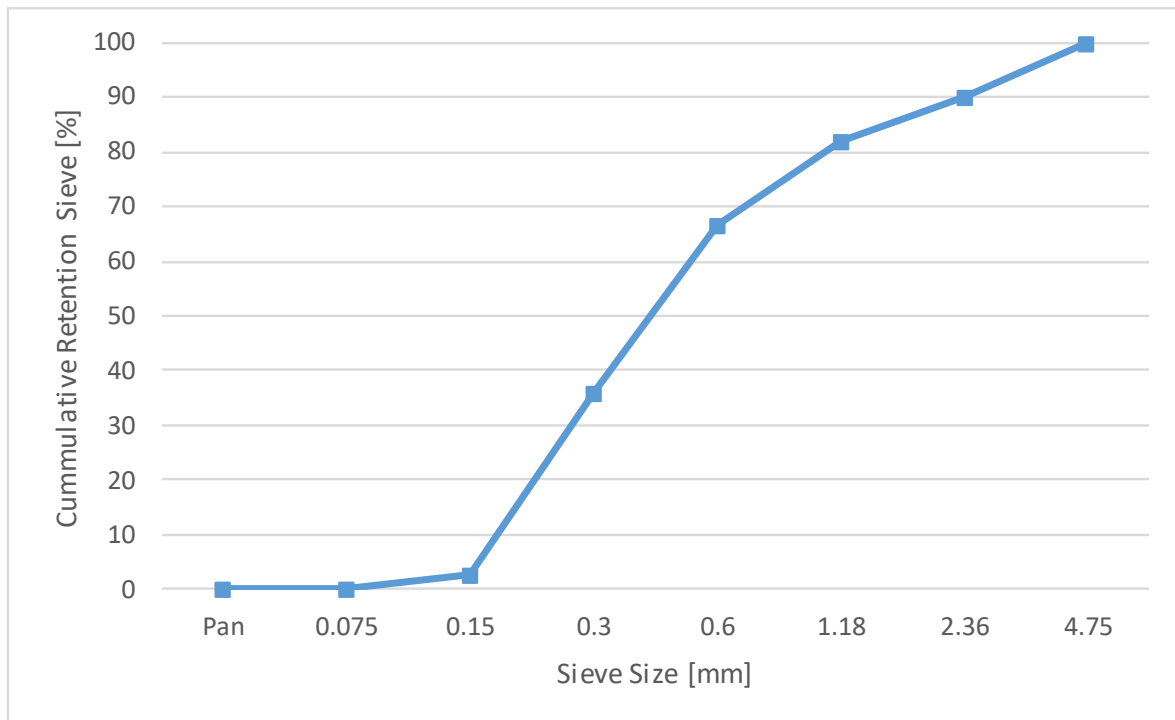


Figure 3.3: Grading of sand used in this study

### 3.2.5. Water

Distilled water, prepared through the purification process of reverse osmosis, was used in this study. This decreases the possibility of fluctuations in the mineral composition of the water and the influence thereof.

### 3.2.6. Superplasticisers

In this study, four different superplasticisers were considered, three PCE- and one SNF based.

The first polycarboxylic ether (PCE) based superplasticiser, referred to as SP1 in this study, is commercially known as CHRYSO Premia 196. This PCE is classified as high range water reducing superplasticising admixture and is part of the CHRYSO Fluid Premia range of superplasticisers. This range is aimed at self-compacting concrete, specifically in the precast industry. The Premia range is claimed to offer superplasticisers with very effective water reducing molecules, offering workability retention of between 30 and 45 minutes. This is particularly applicable to the precast industry and the production constraints associated therewith. High early strengths can be achieved while also improving the mould turnaround time which is economically beneficial. The CHRYSO Fluid Premia range also claims to assist in creating a high-quality finish by reducing blemishes, as well as the need for concrete repairs (Chryso, 2019).

The second and third PCEs used in this study is part of the CHRYSO Fluid Optima range, with the second PCE, referred to as SP2 in this study, commercially known as CHRYSO Optima 206 and the third PCE, referred to as SP3, commercially known as CHRYSO Optima 203. The CHRYSO Fluid Optima range of superplasticisers are aimed toward self-compacting concrete, specifically within the ready-mix industry. The Optima range is claimed to assist the ready-mix industry in producing cohesive concrete mixes with thixotropic properties, which describe the ability of becoming less viscous when subjected to an applied force, while also producing a mix design that is robust and non-sensitive, with the ability to easily be implemented while being compatible with the majority of cement types (Chryso, 2019).

Although Optima 203 and Optima 206 are very similar, it was decided to include both in this study as the Optima 206 claims to be compatible with Western Cape cement, while the Optima 203 is believed to be more compatible with low alkali products (Venier A. 2019, personal communication, 9 April).

The fourth superplasticiser, referred to as SP4 in this study, is a naphthalene-based superplasticiser commercially known as CHRYSO Fluid L. Fluid L is claimed to be compatible with all types of Portland cements and is typically used in mixes containing supplementary cementitious materials including blast furnace slag cements, fly ash and silica fume to maintain workability without compromising strength by altering the water-binder ratio (Chryso, 2019).

Table 3.1: Information regarding superplasticisers considered in this study (Chryso, 2019)

	SP1: CHRYSO Premia 196	SP2: CHRYSO Optima 206	SP3: CHRYSO Optima 203	SP4: CHRYSO Fluid L
Relative density	1.055 ± 0.010	1,05 ± 0,02	1.04 ± 0.01	1.2
PH	7,5 ± 2,0	7 ± 2	7 ± 2	7
Min dosage	0.3165%	0.315%	0.312%	0.72% (as guide, site trials recommended)
Max dosage	3.165%	3.15%	3.12%	2.4% (as guide, site trials recommended)

It should be mentioned that more information on the chemical composition and polymer structures of especially the PCE superplasticisers is not known. At the time of writing this thesis, the manufacturer was not willing to provide this information. This is unfortunate since it is important to know the differences in especially the PCE superplasticisers. However, for this study, the commercial names and application description as mentioned previously is believed to be adequate in identifying compatibility issues.

### 3.3. Characterisation of dry materials

As this study focusses on the interaction between different materials, it is of importance to characterise the materials used, both physically as well as chemically. This could help shed light on the outcome of the results as well as give insight into why certain materials interact differently than others.

To characterise the materials physically, a surface area analysis and a particle size distribution were done, together with a Scanning Electron Microscope (SEM) images to determine the shape and roughness of the particles.

While X-ray fluorescence (XRF) analysis was conducted on the samples to determine the chemical composition thereof, as well as Energy Dispersive X-ray spectroscopy (EDS) analysis to visually demonstrate the difference in the materials' chemical structures.

#### 3.3.1. Surface area

Table 3.2 depicts the surface area of the different samples, obtained by using the ToniPERM, which determines these values based on the Blaine fineness test, in accordance with SANS 50196-6 (2014). The ToniPERM, seen in Figure 3.4, is an automatic air permeability tester used to determine the specific surface area, also known as the Blaine value, of powdered material.



Figure 3.4: ToniPERM used to determine surface area

A smaller value indicates a smaller surface area. The larger the surface area, the finer the material. The sand used in this study is not included in the table as the particle size thereof was found to be too large to analyse using this method.

*Table 3.2: Surface area of clinkers, gypsum and bassanite.*

Material	Surface Area [cm <sup>3</sup> /g]
Dwaalboom Clinker	4980
De Hoek Clinker	4635
Slurry Clinker	4950
Bassanite	5505
Gypsum	4800

As seen in Table 3.2, the clinker sourced from the De Hoek plant has a smaller surface area than the other two types, which have similar surface areas. For the three clinkers analysed, a similar fineness was expected due to the milling procedure being identical for each of the clinkers. The difference in the surface area could be a result of a slight inconsistency in the hardness of the various clinkers, with both the Slurry and Dwaalboom clinkers produced in Gauteng and the De Hoek clinker in the Western Cape, resulting in a variation in the raw materials used in the production processes.

Gypsum has a surface area close to that of the clinkers used in this study, while the bassanite has the biggest surface area of all the samples analysed.

### 3.3.2. Particle size

A particle size analysis was done on the different dry materials, to be able to compare the distribution of the various particle sizes of the samples. This analysis makes use of a laser beam which is diffracted when it hits the particles of the sample as it is dispersed into the air, giving a representation of the particle size distribution. The Malvern Mastersizer 2000 (Malvernpanalytical.com, 2019), used to achieve these results, can be seen in Figure 3.5. The smaller the particle size, the larger diffraction angle was achieved.





Figure 3.5: Malvern Mastersizer 2000 used to conduct particle size analysis

The particle size distribution of the various dry materials used in this study can be seen in Figure 3.6 with the results from the analysis being summarised in Appendix C1.

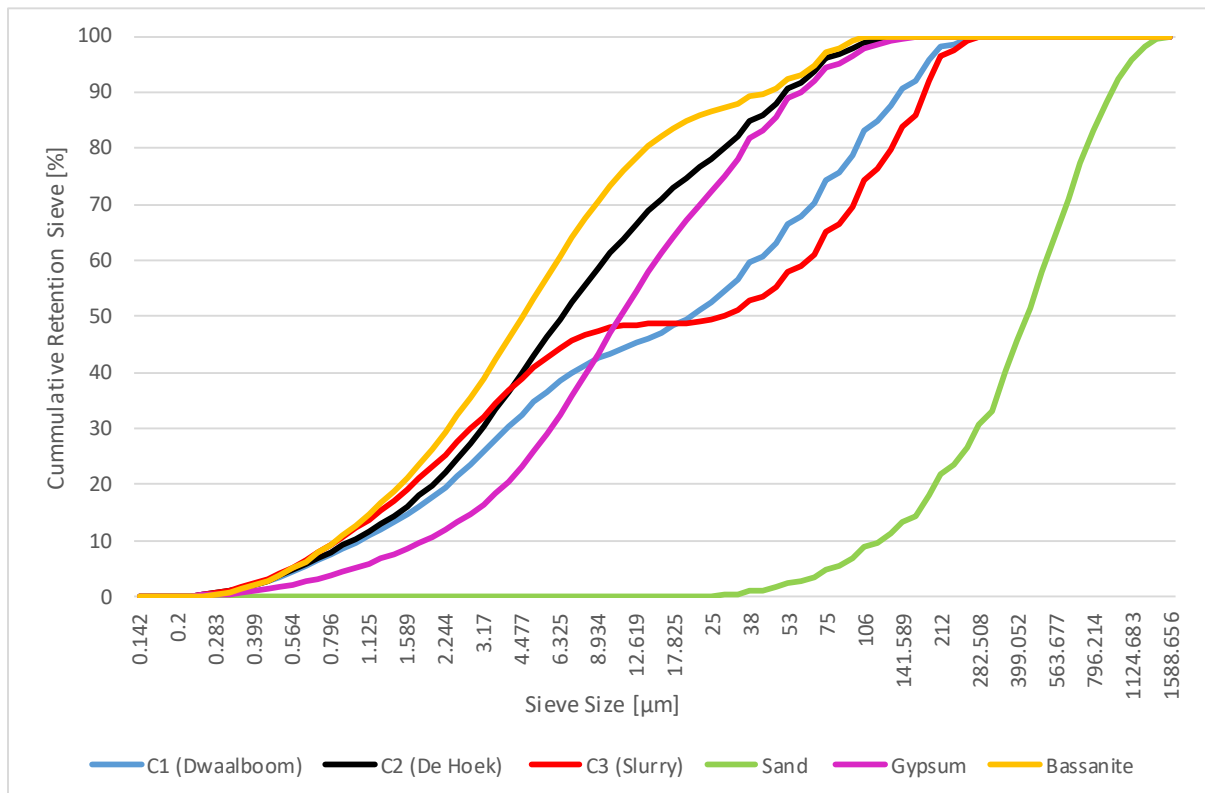


Figure 3.6: Particle size distribution of materials used in this study

From these results, it can be noted that both C1 and C2 have similar particle size distributions, with the particles of C3 being slightly smaller than that of the other two clinkers. The particle size distribution of C3 was however found to be similar to that of the bassanite and gypsum samples. The sand, as expected, was found to have much bigger particle sizes compared to the other materials considered.

The addition of both the bassanite as well as the gypsum can be expected to react similarly with C1 and C2, while a different result would be expected when reacting with C3, when considering only the effect of the particle size on the flowability of a concrete paste, ignoring the influence of the chemical composition of the materials.

### 3.3.3. SEM imaging

SEM images are taken by scanning a focussed beam of high energy electrons over a sample surface, making use of a Zeiss MERLIN SEM (Zeiss.com, 2019). The electrons in the beam interact with atoms in the sample to produce a variety of signals, as some of the electrons are reflected by the specimen while others are absorbed, that contain information regarding the topography of the sample surface. SEM images, as seen in Figures 3.7 to 3.24, were taken of the dry materials used in this study, to provide detail regarding the particle shape and size, while more images can be found in Appendix A.

- C1 (Dwaalboom)

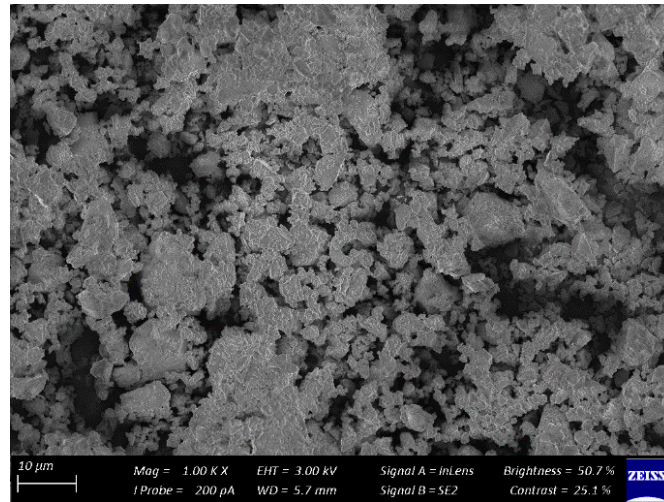


Figure 3.7: SEM image of Dwaalboom clinker [x 1k zoom]

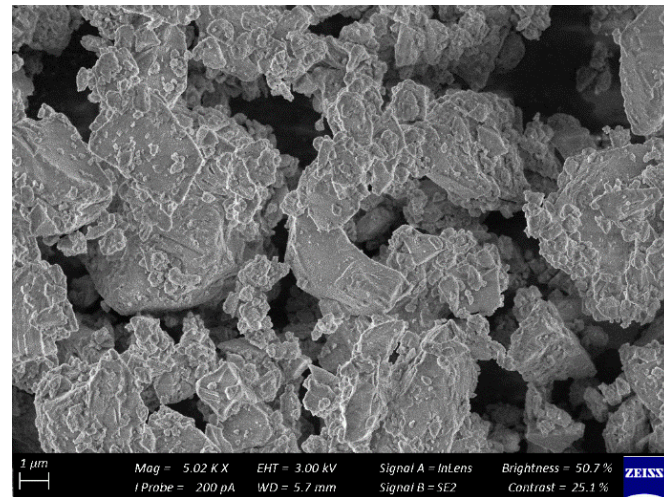


Figure 3.8: SEM image of Dwaalboom clinker [x 5k zoom]

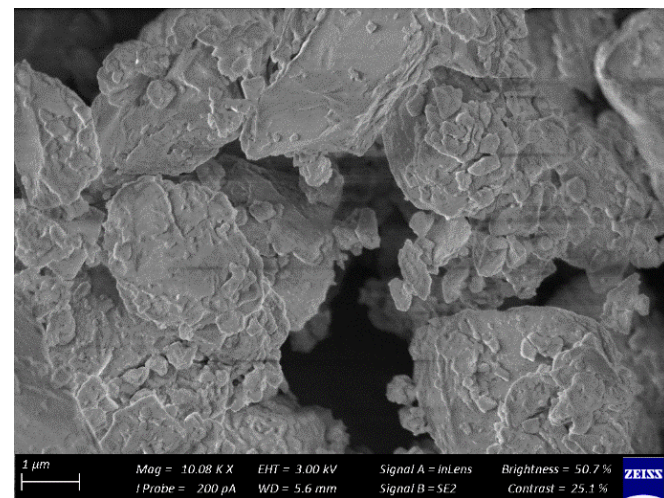


Figure 3.9: SEM image of Dwaalboom clinker [x 10k zoom]



- C2 (De Hoek)

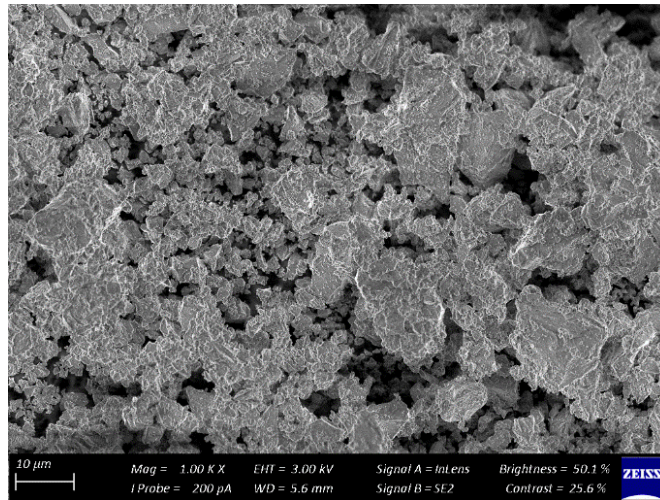


Figure 3.10: SEM image of De Hoek clinker [x 1k zoom]

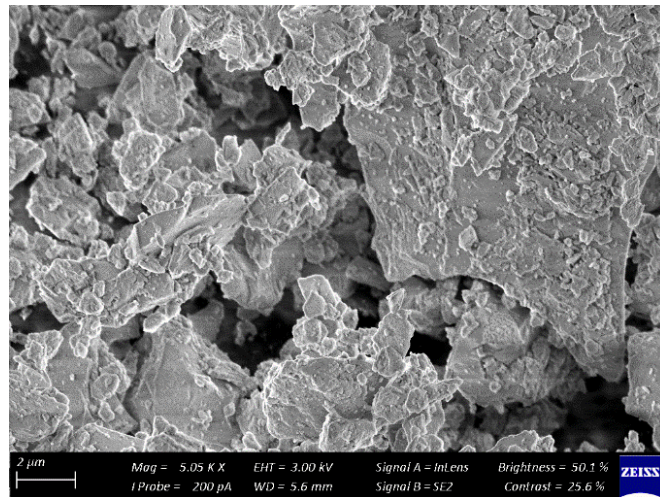


Figure 3.11: SEM image of De Hoek clinker [x 5k zoom]

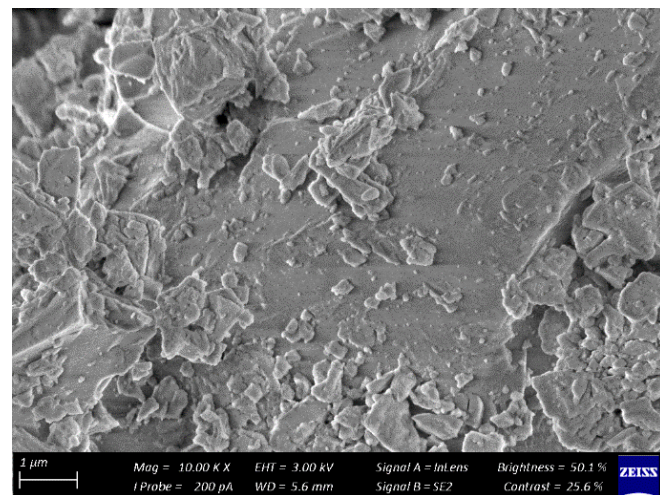


Figure 3.12: SEM image of De Hoek clinker [x 10k zoom]

- C3 (Slurry)

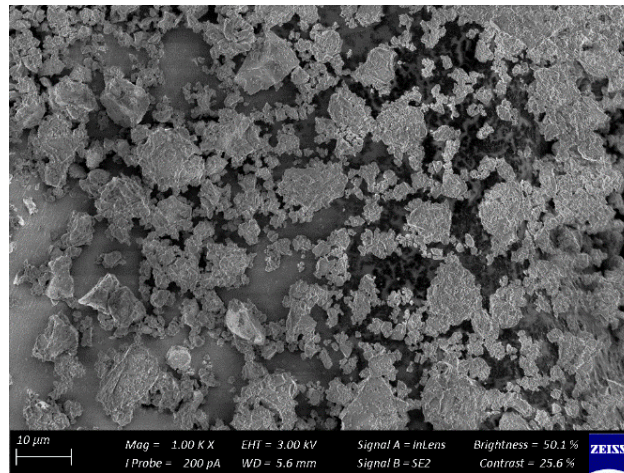


Figure 3.13: SEM image of Slurry clinker [x 1k zoom]

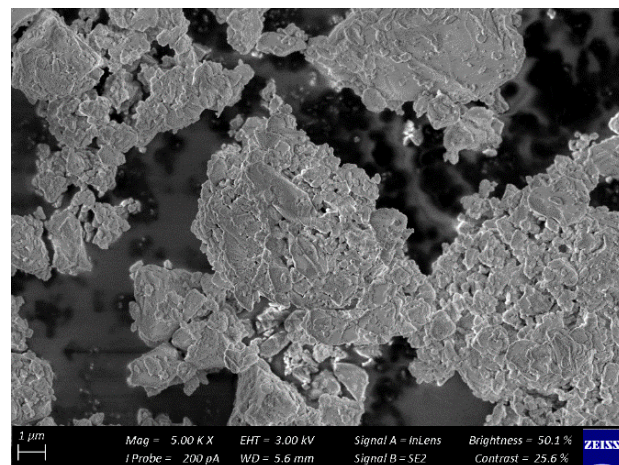


Figure 3.14: SEM image of Slurry clinker [x 5k zoom]

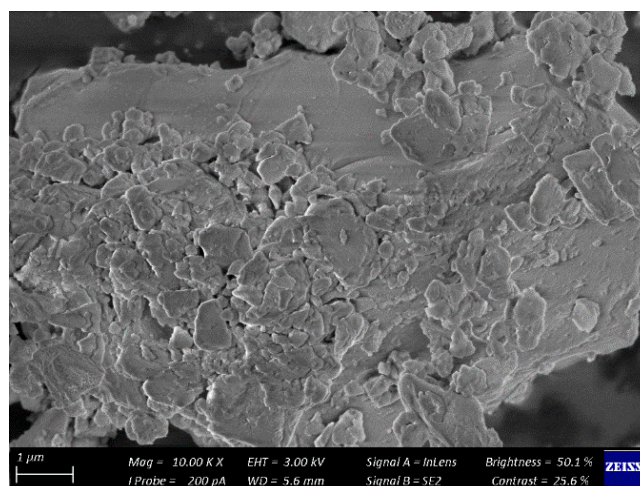


Figure 3.15: SEM image of Slurry clinker [x 10k zoom]



- G1 (Bassanite)

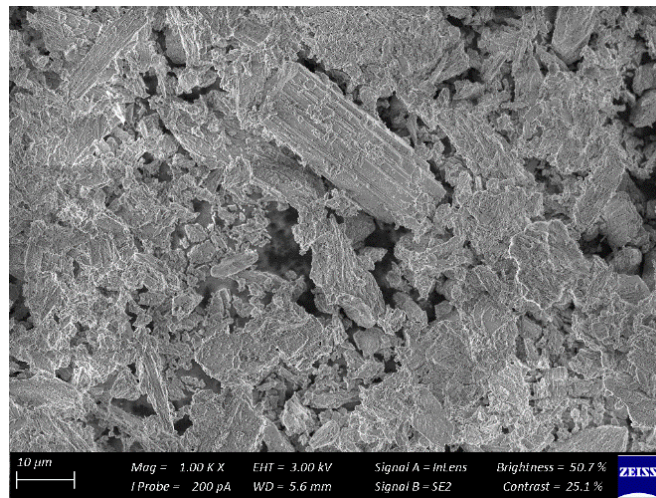


Figure 3.16: SEM image of Bassanite [x 1k zoom]

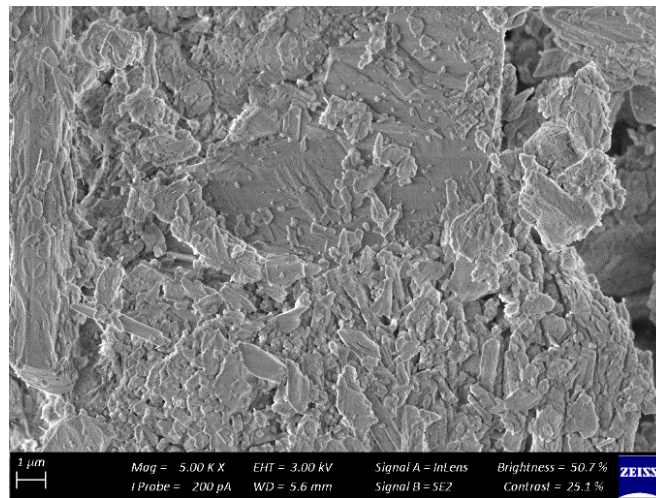


Figure 3.17: SEM image of Bassanite [x 5k zoom]

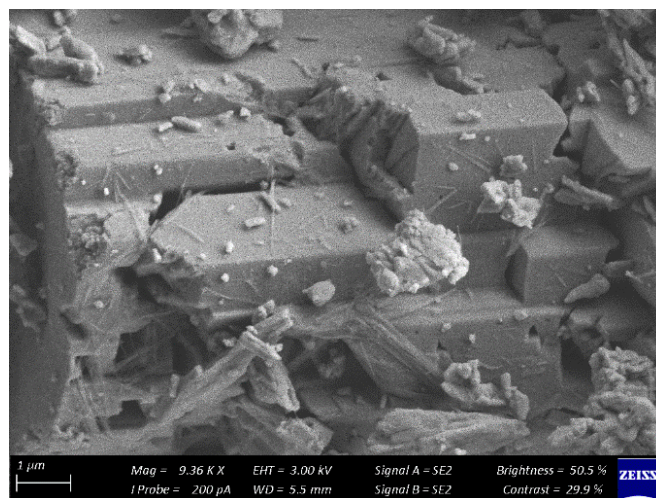


Figure 3.18: SEM image of Bassanite [x 9.36k zoom]

- G2 (Gypsum)

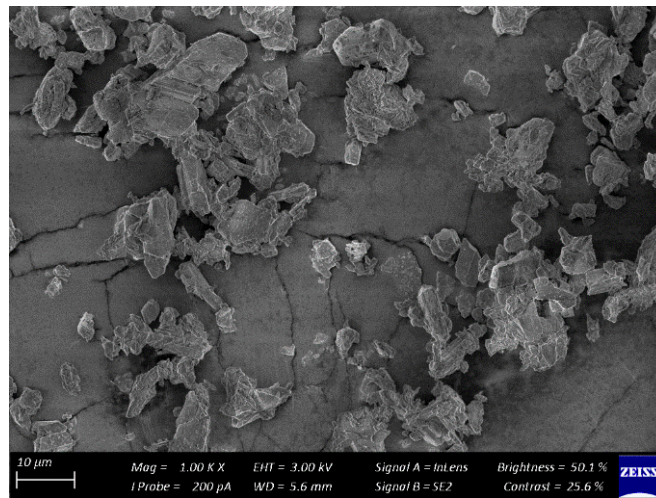


Figure 3.19: SEM image of Gypsum [x 1k zoom]

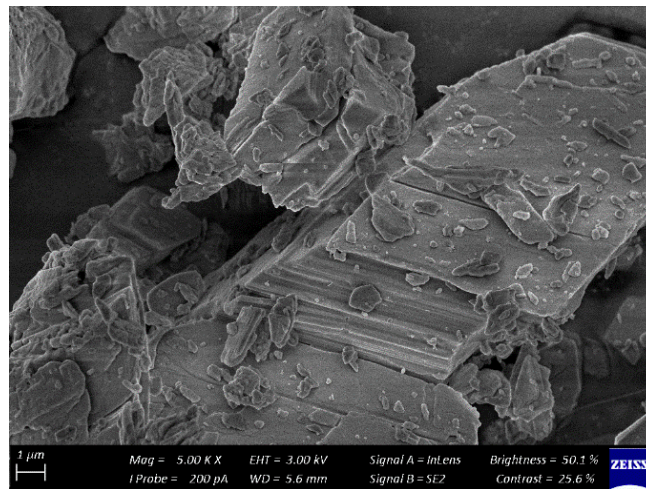


Figure 3.20: SEM image of Gypsum [x 5k zoom]

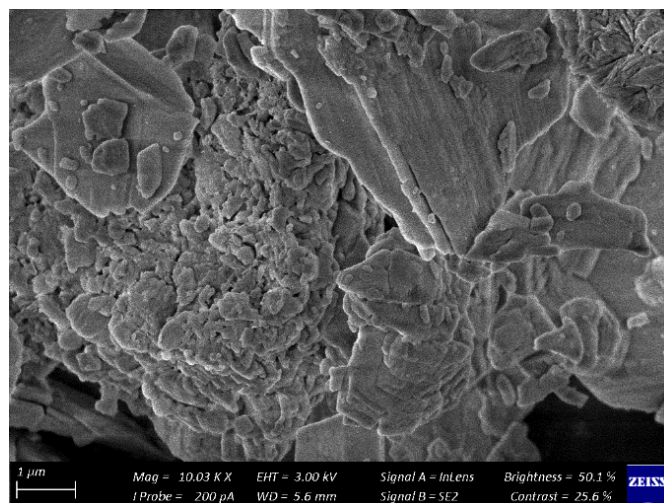


Figure 3.21: SEM image of Gypsum [x 10k zoom]



- Sand

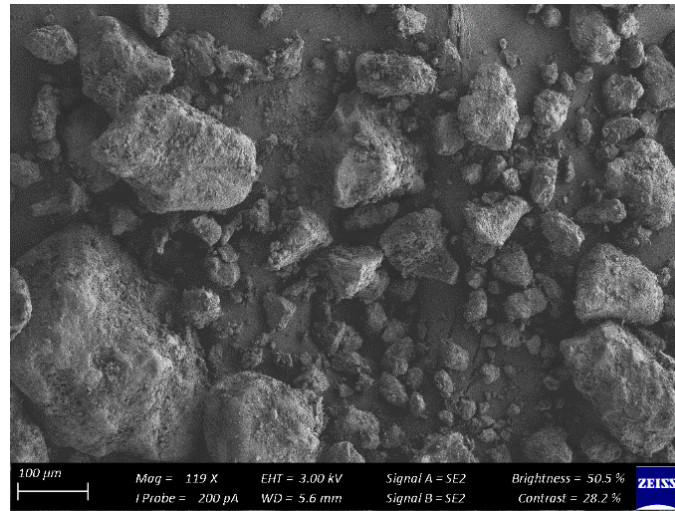


Figure 3.22: SEM image of Sand [x 119 zoom]

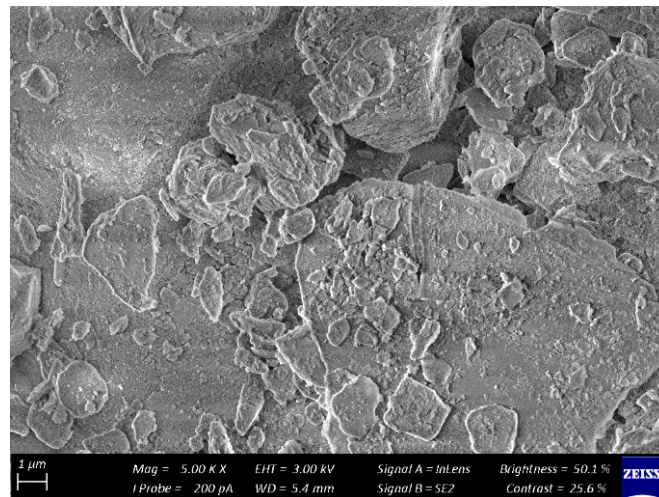


Figure 3.23: SEM image of Sand [x 5k zoom]

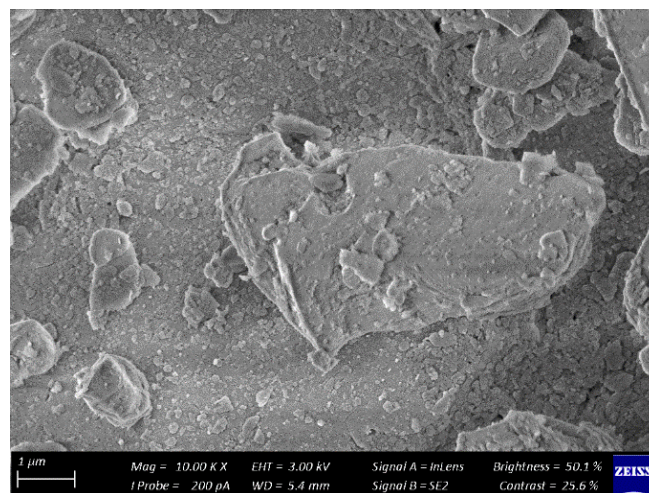


Figure 3.24: SEM image of Sand [x 10k zoom]



From Figures 3.7 to 3.15 showing the particles of the various clinkers, as expected due to the similar milling process, it can be seen that the different clinkers have a similar particle shape and size. In addition, all the different clinkers show a rough, shredded finish to the particle, assumed to be a result of the milling process. The gypsum and bassanite are shown to have a similar particle shape and size. Although they also have a rough surface, it is more angular and cubed shape than that of the clinkers, suggesting the particles broke during the milling process instead of being torn, as the case with the clinker particles. The sand has a much bigger particle size than that of the other materials considered, and although the sand also shows a rough surface, the particle shape thereof is much smoother with an overall more coherent shape.

The particle shape and size of the clinkers and sulphates are similar and is therefore not expected to significantly influence the flowability and behaviour of the pastes with respect to each other. This suggests that the chemical aspect of the materials should be considered as the main aspect influencing the flowabilities and behaviour of the pastes.

#### 3.3.4. Elemental analysis

The chemical composition of the samples plays a vital role in this study, especially determining the different amounts of  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  present in the clinker. It is also necessary to establish the difference in the chemical composition of the gypsum and the bassanite, to be able to better understand the reaction between the materials. Two types of analysis were done to help characterise the different samples chemically, X-ray fluorescence (XRF) and Energy-dispersive X-ray spectroscopy (EDS) analysis, as discussed in the following sections.

##### 3.3.4.1. XRF analysis

The XRF analysis makes use of x-rays to energize atoms of a sample. A high energy x-ray is used to irradiate the specimen sample. When an atom is struck by an x-ray beam, with enough energy, an electron from the inner orbital shells is dislodged and elevated to a higher orbital shell. For the atom to regain stability, an electron from one of the atom's higher energy orbitals falls to a lower energy state to fill the vacancy that is left in the inner orbital shell. To achieve this, the electron from the higher energy orbital emits a fluorescent x-ray, to drop to a lower energy state. The x-ray released by the atom during this process is equal to the specific difference in energy between two quantum states of the electron (Thermofisher.com, 2019) and can thus be used to identify different elemental components of the specimen. Figure 3.25 illustrates the concept on which the XRF analysis is based while Table 4.4 contains the results obtained during the analysis.

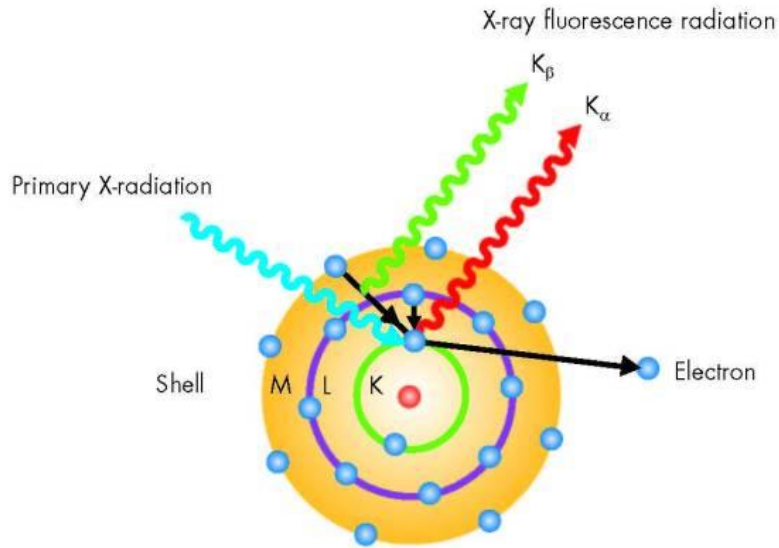


Figure 3.25: Illustration of the principle on which XRF analysis is based (XRF Spectroscopy, 2019)

The XRF analysis, performed using the ARL 9900 XP - XRF spectrometer (ThermoFisher.com, 2019), supplied by ThermoFisher, was used to obtain the elemental results shown in Table 4.4, it does however not indicate the amount of  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  components present in the sample. The respective  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  contents of the three different clinkers can be calculated by using the Bogue equations (Winter, 2009). The mathematical formulas associated with this calculation are as follows (Winter, 2009).

Equation 3.1-3.4: Bogue calculations

$$C_2S = (SiO_2 * 2.867) - (0.754 * C_3S)$$

$$C_3A = ((Al_2O_3 + TiO_2 + P_2O_5) * 2.65) - ((Fe_2O_3 + Mn_2O_3) * 1.692)$$

$$C_3S = (4.071 * (CaO - FCaOResult)) - 7.6024 * (SiO_2) - (6.718 * (Al_2O_3 + TiO_2 + P_2O_5)) - (1.43 * (Fe_2O_3 + Mn_2O_3))$$

$$C_4AF = (Fe_2O_3 + Mn_2O_3) * 3.043$$

#### 3.3.4.2. EDS analysis

Similar to the method of the XRF analysis, the atoms on the surface of a sample are elevated to an excited state. Typically integrated into a SEM instrument, again using the Zeiss MERLIN SEM (Zeiss.com, 2019), the electron beam from the SEM excites the atoms of the specimen, when these atoms return to their natural state, they emit an x-ray which is characteristic to a certain element. These x-rays are gathered by a detector built into the instrument and converted into information regarding the elemental composition of the sample area. The results for this analysis can be seen in Appendix B and is only used as a visual representation to validate the results obtained through the XRF analysis.

### 3.4. Mix designs

In this study, three principle mixes were considered which were altered to create 114 different mixes for testing. A reference mix, that was tested three times for each test to establish whether the results obtained could be repeated, was used as the basis of all mix designs.

The first alteration to the reference mix was by adding various dosages of different superplasticisers as an addition to the water content while keeping the water-binder ratio the same. For every increasing dosage, a new batch was used for testing to eliminate any irregularities in the testing circumstances.

Thereafter, the reference mix was altered with the addition of either gypsum or bassanite. These additions were added as a binder substitution to maintain a constant water-binder ratio. Again, as with the superplasticiser dosages, a new batch was used for every addition considered.

Finally, a combination of various dosages superplasticisers was considered with different additions of gypsum and bassanite respectively. This was done to establish a variation in the reactions between the superplasticisers and the different clinkers when used in the presence of a sulphate source.

The same mix design was used when conducting the Marsh cone, mini slump and strength tests, however, a different mix closely related to that as specified in the setting times standard (SANS 50196-3:2006), was used when determining the setting times. The motivation for using an alternative mix design to determine the setting times came when the setting times for various standard mixes containing C1 (Dwaalboom clinker) exceeded 18 hours. The mixing proportions for the principle mixes, as used for the Marsh cone, mini slump and strength tests, are shown in Table 3.3. The mix design as used to determine the setting times can be seen in Table 3.4. The mix designs are discussed in further detail in the following sections.

Table 3.3: Mix design for Marsh cone, mini slump and strength tests

	Mix					
	Reference	SP	Bassanite	Gypsum	Bassanite + SP	Gypsum + SP
Material	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]
Sand	1043.5	1043.5	1043.5	1043.5	1043.5	1043.5
Water	347.8	347.8	347.8	347.8	347.8	347.8
Clinker	695.7	695.7	681.7 / 667.8 / 653.9	681.7 / 653.9	681.7 / 667.8 / 653.9	681. / 653.9
Bassanite	-	-	13.9 / 27.8 / 41.7	-	13.9/ 27.8 / 41.7	-
Gypsum	-	-	-	13.9 / 41.7	-	13.9/ 41.7
SP	-	1.4 / 3.5 / 6.3	-	-	1.4 / 3.5 / 6.3	6.3

For the mix design used to determine the setting times, both the superplasticiser as well as the bassanite/gypsum additions were kept the same as in the mix design in Table 3.3. The sand was however removed and the water content reduced, resulting in a water-binder ratio of 0.27, which is similar to that used by cement manufacturers (Physical Tester at PPC De Hoek, 2019, personal communication) when conducting setting time tests (SANS 50196-3:2006).

Table 3.4: Mix design for setting time tests

	Mix					
	Reference	SP	Bassanite	Gypsum	Bassanite + SP	Gypsum + SP
Material	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]
Water	78.3	78.3	78.3	78.3	78.3	78.3
Clinker	289.9	289.9	284.1/ 278.3 / 272.5	284.1/272.5	284.1/ 278.3 / 272.5	284.1/272.5
Bassanite	-	-	5.8 / 11.6 /17.4	-	5.8 / 11.6 /17.4	-
Gypsum	-	-	-	0.58 / 2.6	-	0.58 /2.6
SP	-	0.58 / 1.4 / 2.6	-	-	0.58 / 1.4 / 2.6	2.6

#### 3.4.1. Reference mixes

Three reference mixes were designed by making use of a method of trial and error, keeping in mind the requirements and limitations of the test procedures. The reference mixes consist only of Clinker 1, 2 and 3 respectively as well as sand and water.

For two of the clinkers considered, the reference mix did not flow through the Marsh cone, this could have been rectified by increasing the water content of the reference mix. However, during initial tests, the addition of superplasticisers caused segregation due to the high water content and superplasticiser. This would have compromised the findings of this study as one could not identify segregation as a compatibility issue and therefore the reference mixes were not changed.

With the addition of gypsum and bassanite, the workability of the mix decreased. However, the water content was again not lowered, resulting in mixes that did not completely flow through the Marsh cone, leaving some of the paste to remain in the cone. Although these mixes did not empty the cone as specified by the Marsh cone standard, information could still be gathered on the flowability of these mixes, by considering the time that continuous flow lasted as well as how much of the paste was found remaining in the Marsh cone after testing.

#### 3.4.2. Mixes with superplasticiser

For these mixes, varying dosages of the four different superplasticisers were added to the reference mixes, with the dosages being either 0.2%, 0.5% or 0.9% of the binder content. This was done to determine the influence of the different superplasticisers with the different clinkers at a low-,

medium- and high dosages of the superplasticiser on the chemical compositions of the three clinkers. The superplasticiser was added to the water and did not replace a percentage thereof in an attempt to keep the water binder ratio constant.

### 3.4.3. Mix with bassanite/gypsum

Bassanite and gypsum, respectively, were added to the reference mixes as substitution of a percentage clinker. Both substitution and addition were considered in initial tests, after which it was decided to use substitution to keep the water-binder ratio constant throughout this study.

A thermogravimetric analysis was done, according to a method used by PPC to determine if prehydration of cement has occurred during the milling of the cement (Senior analyst at PPC De Hoek, 2019, personal communication), on a sample of both the bassanite and gypsum used in this study to determine the pre-hydration of the materials. According to this procedure, the weight loss of a sample at different temperatures is determined. The weight loss of the sample, when heated to 110 °C, is due to the loss of water being evaporated while the weight loss of the sample when heated to 150 °C from 110 °C is due to the loss of water from the dehydration of gypsum. This analysis was used to determine the chemical formula of both the bassanite as well as the gypsum, to compare it with the chemical formula of gypsum typically found in cement.

The gypsum was found to have a composition of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  while bassanite was found to have the composition of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  which is a lower water content than the gypsum used in this study. During the grinding process of clinker, heat is generated in the mill causing the gypsum to be partly dehydrated, forming hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) (Winter, 2009). Since the chemical formula of the bassanite is more similar to that of gypsum found in cement it was decided to use bassanite as the main addition in this study, while only doing a few tests incorporating the gypsum. This was due to limitations on the amounts of clinker being available and therefore the number of tests that could be conducted.

The gypsum typically found in cement has a composition consisting of 70% bassanite as  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and 30% gypsum as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . This is due to the temperatures in the finishing mill resulting in a loss of moisture (Winter, 2009).

Cement manufacturers use the percentage  $\text{SO}_3$  available in the clinker, as well as the amount of  $\text{SO}_3$  present in the gypsum, to calculate the gypsum requirement of the cement. For C1 (Dwaalboom clinker), the optimal  $\text{SO}_3$  content varies between 1.6% and 2.6% while C2 (De Hoek clinker) has an optimal  $\text{SO}_3$  content between 2% and 2.5%. For C3 (Slurry clinker), the optimal  $\text{SO}_3$  content ranges from 1.3%, 1.6% and 2.1% (PPC Quality Assurance Managers, 2019, personal communication). These

total SO<sub>3</sub> percentages, as provided by the different factories, differ between the three plants as they produce types of cement from different sources of raw materials (limestone and clay). An average total SO<sub>3</sub> percentage of 1%, 2% and 3% is used in this study to accommodate the different clinkers and applications associated with them. Subsequently, the addition of bassanite/gypsum to the clinker was needed to be determined to supplement the SO<sub>3</sub> levels of the clinker to reach the desired total percentage SO<sub>3</sub>.

A wet analysis was done according to SANS 50196-2 (2014) to determine the SO<sub>3</sub> content of the different clinkers, as well as the bassanite and gypsum, which was then used in the formulas that can be found in Appendix C2, used and supplied by PPC, to determine the optimal bassanite and gypsum addition for each clinker as tabulated in Table 3.5. The results in Table 3.5 was used to calculate the 2%, 4% and 6% bassanite/gypsum addition as an average value to best accommodate all three clinkers while keeping the same percentages for both the bassanite as well as the gypsum

*Table 3.5: Bassanite/Gypsum addition necessary to achieve total SO<sub>3</sub> content*

Total SO <sub>3</sub> content in the mix	1%	2%	3%
	% bassanite/gypsum addition required as binder substitution to achieve total percentage SO <sub>3</sub>		
Dwaalboom clinker/Gypsum	1.74	3.64	5.53
Dwaalboom clinker/Bassanite	1.71	3.56	5.42
De Hoek clinker/Gypsum	0.75	2.66	4.57
De Hoek clinker/Bassanite	0.73	2.60	4.48
Slurry clinker/Gypsum	1.43	3.32	5.22
Slurry clinker/Bassanite	1.4	3.26	5.12

#### 3.4.4. Mix with superplasticiser in combination with bassanite/gypsum

For this part of the study, high- and low dosages of superplasticiser were added to the reference mixes in combination with high- and low quantities of bassanite in an attempt to observe the interaction between bassanite and superplasticiser as well as the effect it has on the chemical composition of the clinkers. As it was only possible to do a limited number of tests with the addition of gypsum, it was decided to only test the interaction between high dosages superplasticiser in combination with high quantities of gypsum.

### 3.5. Test setups

The test setups, according to the appropriate standards for the different tests conducted are explained in the following sections.

#### 3.5.1. Marsh cone

The Marsh cone tests were conducted in accordance with the ASTM C939-10 standard. This standard requires the use of a mixture, containing fine aggregates that pass a 2.36 mm sieve. The fluidity of a liquid grout is to be determined by measuring the time of efflux of a specific volume (1.725 l) of grout by using a standardised flow cone (ASTM: C939-10, 2010). The standard requires a calibration of the flow cone before conducting a test to ensure an accurate result. This calibration involves measuring the flow time of a specific volume (1.725 l) of water. The total time required for the water to pass through the nozzle was specified to be around 8 seconds.

This calibration was verified by measuring the flow time of the water, drained from the flow cone to ensure a constant level of moisture in the cone, before conducting a Marsh cone test. The method described in this standard delivers a result in standard SI units. The dimensions of the stainless-steel flow cone can be seen in Figure 3.26.

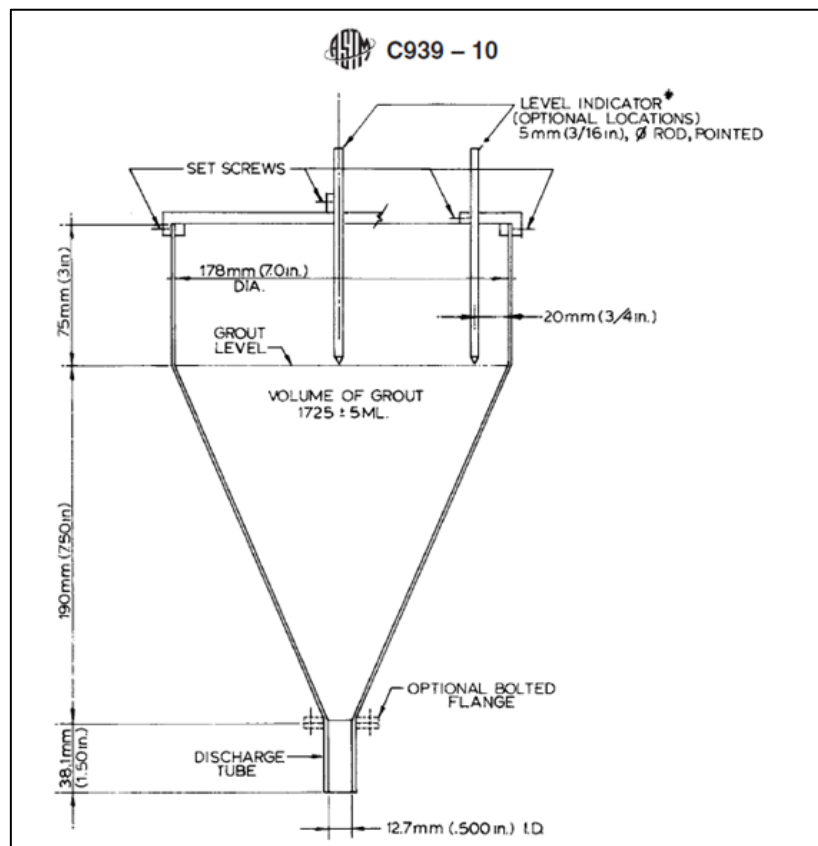


Figure 3.26: Marsh cone dimensions (ASTM: C939-10, 2010).



### 3.5.2. Mini slump

A mini slump cone, as seen in Figure 3.27, with dimensions according to the same proportions as the slump cone used in accordance with ASTM Test C143 (2015) was used when conducting the mini slump test. The mini slump cone with the following dimensions; top diameter of 20 mm, a bottom diameter of 40 mm and a height of 60 mm was used. A steel plate, marked with a circle diameter as well as vertical, horizontal and diagonal lines according to which the diameter of the mortar mix was measured, was used to simplify the test while keeping the testing procedure constant.

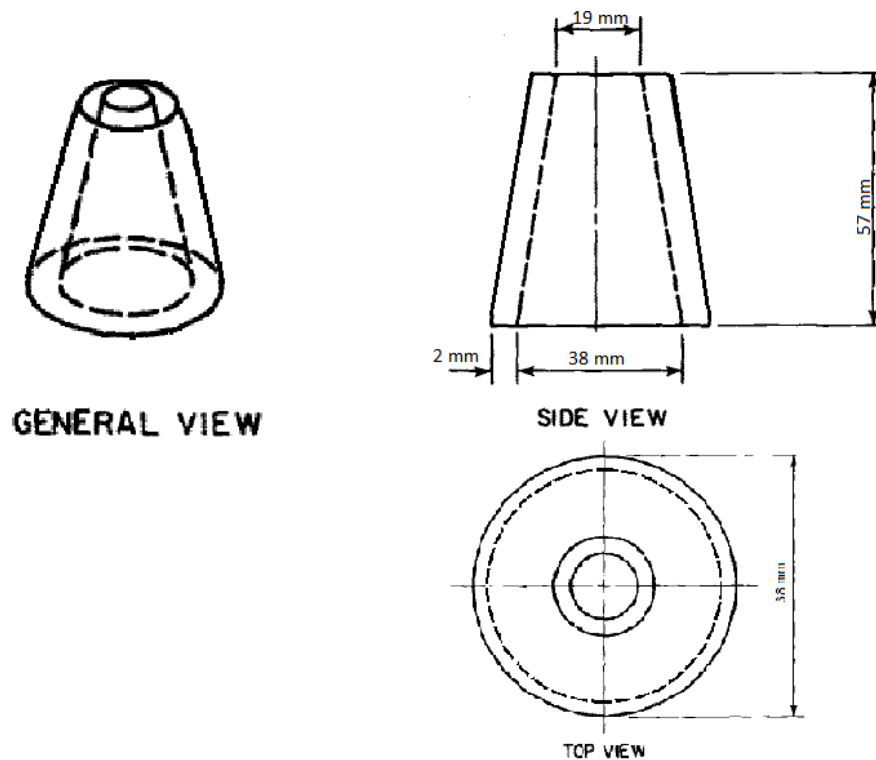


Figure 3.27: Mini slump dimensions (ASTM Test C143, 2015)

### 3.5.3. Strength

The casting, demoulding, curing and breaking of the prisms to determine the characteristic strength of a mix design was done in accordance with the SANS 50196-1 (2006) standard. The mix content, as well as the mixing procedure, was however not in compliance with the standard. The mix used in the Marsh cone- and the mini slump tests were re-used in the strength tests. This was done to save on the materials being used. Only a limited amount of clinker was available to be used in this study, it was decided to prioritise the number of mixes tested, as this has a greater impact on the outcome of the study. The strength test results do however remain comparable to each other and can give an indication on how the additions influence the strength of the paste at 2- and 7 days.

### 3.5.4. Setting times

During this study, the mixing procedure followed when determining the setting times of a paste, was done in accordance with the mixing procedure explained in EN 196-3:2005. Both the initial- and final setting times were then recorded by an automated Vicat needle instrument, calibrated according to EN 196 and ASTM C 191 for use on cement pastes.

### 3.6. Testing procedure

The procedure followed for the various mixes as well as the different test setups is discussed in the following sections.

#### 3.6.1. Mix procedure for Marsh cone, mini-slump and strength tests

For the mix used to conduct the Marsh cone test, the mini slump test as well as the strength tests, the following method was followed:

In a 10 l cement mixer, as seen in Figure 3.28, the binder mix (either only containing clinker or a combination of clinker and gypsum/bassanite) was mixed with the sand for one minute at a speed of 62 rpm. 90% of the water content, 540 ml, (containing the superplasticiser if applicable) was added and mixed for 2 minutes after which the remaining 10% of the water was added. After 4 minutes, the mixer was stopped, and the sides and bottom of the mixer were scraped using a spatula. The mix was then allowed to mix for another 6 minutes, resulting in a total mixing time of 10 minutes, with a mixing time of 9 minutes since the addition of liquids to the dry materials.



Figure 3.28: Cement mixer used in this study

The Marsh cone nozzle was blocked with a rubber stopper and filled with 1.725 l of water. When the timer, as seen on Figure 3.29, reached 9 minutes after starting mixing, 1 minute before the end of the mixing time, the rubber stopper was removed, and the Marsh cone, as seen in Figure 3.30, was left to run dry. At 20 seconds before the 10-minute mixing mark, the rubber stopper was placed back in the Marsh cone and a spirit level was used to ensure the cone was placed level in the stand. This was done to keep the cone consistently moist throughout the testing procedure.

At the 10 minute total mixing time, the mixture is poured into the cone up until the 1.725 l mark. The rubber stopper is then removed while simultaneously starting the timer. The timer was stopped when either the total volume of the mix passed through the cone, or when the continuous stream was broken.



Figure 3.29: Timer used in this study



Figure 3.30: Marsh cone used in this study

After conducting the first Marsh cone test, the mix was also used to perform the mini slump test. The mini slump cone, as seen in Figure 3.31, was filled, parallel to the brim of the cone, with the mixture, where after the cone was gently lifted in a continuous upward motion. A minute after removing the cone, the diameter of the mix was measured with a steel ruler in four directions, of which the average

is calculated. This result would then be tabulated as the first mini slump test result at a time referred to as after 0 minutes.



*Figure 3.31: Mini slump cone used in this study*

After conducting both the Marsh cone and the mini slump test, the mix was placed back into the mixer to be continuously mixed for another 20 minutes, repeating the mini slump procedure described, at time 20 minutes, 40 minutes and 60 minutes after the first Marsh cone test was performed. When all the tests conducted on a mix was completed, the mixture was used to cast into prisms for compression strength tests.

The moulds were filled in accordance with SANS 50196-1. Moulds, as seen in Figure 3.32, are primed with demoulding oil and placed on a vibrating table, as seen in Figure 3.33, for two minutes after which the excess oil is removed from the mould. The vibrating table is started again, and the mix is scooped into the moulds for a total of 15 seconds and left to vibrate for 15 seconds before adding the rest of the mixture. After 2 minutes on the vibrating table, the excess mortar is scraped from the moulds.



*Figure 3.32: Moulds used to cast prisms for strength tests*



*Figure 3.33: Vibrating table used in this study*



The moulds, filled with the mixture, is covered with a rubber lining and plastic sheet, as seen in Figure 3.34, and placed into a curing room as in Figure 3.35. After 24 hours, the prisms are demoulded, marked, and placed in curing tanks where until testing.



*Figure 3.34: Rubber and plastic used to cover the moulds whilst curing*



*Figure 3.35: Filled moulds in the curing room*

After, either 2 or 7 days, the prisms are removed from the curing tanks, dried, weighed, and split into 2 cubes, as seen in Figure 3.36. These cubes are then placed in ToniPRAX, a test machine used for the standard-compliant testing of the compressive and flexural strength of cement and other binding materials (Tonitechnik, 2019) as seen in Figure 3.37, where it is then crushed to determine the tensile

strength of the cube according to EN 196 / ISO 679 (2009). The average of four results is considered to determine a representative result.



Figure 3.36: Breaking of prisms in half in order to conduct strength tests



Figure 3.37: ToniPRAX used to determine compressive strength of prisms

For the 2-day strength test, the cubes were tested within 30 minutes before or after 2 days when water was first added to the mix. This time is increased to 2 hours before- or after the initial mixing time when testing the seven-day strengths.

### 3.6.2. Mix procedure for setting time test

For the mix used to determine the setting time, the water (or if applicable, the water and superplasticiser) was added to the 10 l cement mixer, after which the dry materials are added. The time of addition is noted. The mixture is mixed at a speed of 62 rpm for 90 seconds after which the mixer is stopped for a total of 30 seconds, to remove the paste adhering to the sides and the bottom of the bowl with a spatula. The mixer is again started for another 90 seconds, resulting in a total mixing time of 3 minutes. After the mixing procedure is completed, moulds, as pictured in Figure 3.38, that had been primed with demoulding oil, is filled to the brim with the mortar paste and levelled off. The mould is then placed into the ToniSet Compact, seen in Figure 3.39, an automated Vicat needle instrument, based on SANS 50196-3 (2006), to determine the initial and final setting time of the paste. The ToniSet compact is computer controlled and is used to determine the setting characteristics of cement and gypsum respectively (Tonitechnik, 2019). The time of contact between the dry- and wet materials are inserted into the ToniSet Compact where after a reading is taken at regular intervals until the time initial and final set is achieved. This interval changes as the depth of the measurement varies to ensure an accurate result.



Figure 3.38: Moulds used when determining setting times



Figure 3.39: ToniSet Compact used to determine setting times

Furthermore, all materials were weighed by using a digital scale, as seen in Figure 3.40, measuring up to three decimal places in grams. The bassanite/gypsum was added to the clinker and homogenised by making use of a turbula mixer, as seen in Figure 3.41, before introducing it into the mixture.



Figure 3.40: Scale used in this study

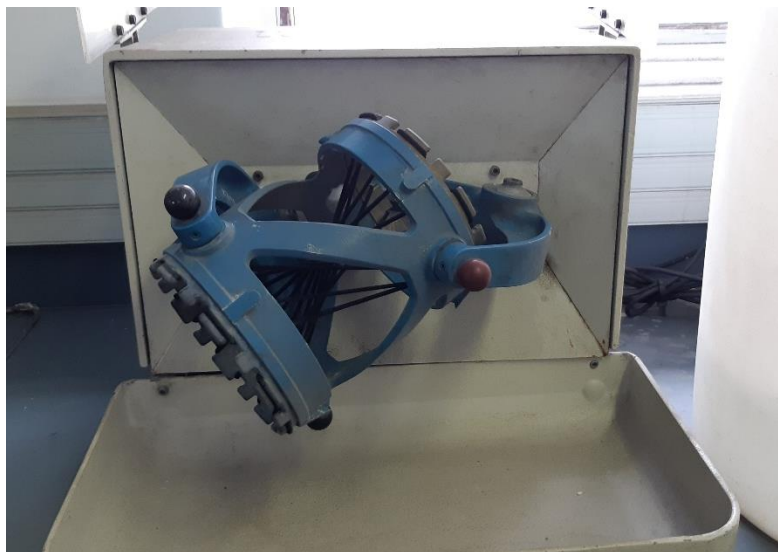


Figure 3.41: Turbula mixer



### 3.7. Test program

To achieve the objectives, set out for this study, mixes were designed in such a way to be able to observe the interaction between the different clinkers, bassanite, gypsum and the four different superplasticisers.

A summary of all the mixes considered in this study is tabulated in Table 3.6. For each of the mixes, the Marsh cone- as well as the mini slump test was conducted at 0-, 20-, 40- and 60 minutes after which the mix was used to cast prisms to be used in the strength tests. The setting times of each of the mixes was also determined.

The reference mix for each of the three clinkers was repeated three times, to be able to determine the reliability of the results obtained. For all the other mixes considered in this study, only one test was conducted.

In this table, C1 refers to the Dwaalboom clinker with a high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content, C2 refers to the De Hoek clinker with medium  $C_3S$ ,  $C_2S$  and  $C_3A$  and low  $C_4AF$  content and C3 to the Slurry clinker with high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  content. G1 refers to the bassanite – and G2 to the gypsum additions considered in this study.

SP1 refers to superplasticiser 1; a general PCE based superplasticiser. SP2 refers to Superplasticiser 2; a PCE based superplasticiser designed to be compatible with Western Cape cements and SP3 refers to Superplasticiser 3; a PCE designed to be more compatible with low alkali cements. SP4 refers to Superplasticiser 4 which is a naphthalene-based product.

Table 3.6: Summary of mix designs for tests conducted

Reference mixes with only Clinker	Mixes with Superplasticiser	Mixes with Bassanite/Gypsum	Mixes with Bassanite and Superplasticiser	Mixes with Gypsum and Superplasticiser
C1	C1 + 0.2% SP1	C1 + 2% G1	C1 + 0.2% SP1 + 2% G1	C1 + 0.9% SP1 + 6% G2
C1	C1 + 0.5% SP1	C1 + 4% G1	C1 + 0.9% SP1 + 2% G1	C1 + 0.9% SP2 + 6% G2
C1	C1 + 0.9% SP1	C1 + 6% G1	C1 + 0.2% SP2 + 2% G1	C1 + 0.9% SP3 + 6% G2
C2	C1 + 0.2% SP2	C2 + 2% G1	C1 + 0.9% SP2 + 2% G1	C1 + 0.9% SP4 + 6% G2
C2	C1 + 0.5% SP2	C2 + 4% G1	C1 + 0.2% SP3 + 2% G1	C2 + 0.9% SP1 + 6% G2
C2	C1 + 0.9% SP2	C2 + 6% G1	C1 + 0.9% SP3 + 2% G1	C2 + 0.9% SP2 + 6% G2
C3	C1 + 0.2% SP3	C3 + 2% G1	C1 + 0.2% SP4 + 2% G1	C2 + 0.9% SP3 + 6% G2
C3	C1 + 0.5% SP3	C3 + 4% G1	C1 + 0.9% SP4 + 2% G1	C2 + 0.9% SP4 + 6% G2
C3	C1 + 0.9% SP3	C3 + 6% G1	C1 + 0.2% SP1 + 6% G1	C3 + 0.9% SP1 + 6% G2
	C1 + 0.2% SP4	C1 + 2% G2	C1 + 0.9% SP1 + 6% G1	C3 + 0.9% SP2 + 6% G2
	C1 + 0.5% SP4	C1 + 6% G2	C1 + 0.2 SP2 + 6% G1	C3 + 0.9% SP3 + 6% G2
	C1 + 0.9% SP4	C2 + 2% G2	C1 + 0.9% SP2 + 6% G1	C3 + 0.9% SP4 + 6% G2
	C2 + 0.2% SP1	C2 + 6% G2	C1 + 0.2% SP3 + 6% G1	
	C2 + 0.5% SP1	C3 + 2% G2	C1 + 0.9% SP3 + 6% G1	
	C2 + 0.9% SP1	C3 + 6% G2	C1 + 0.2% SP4 + 6% G1	
	C2 + 0.2% SP2		C1 + 0.9% SP4 + 6% G1	
	C2 + 0.5% SP2		C2 + 0.2% SP1 + 2% G1	
	C2 + 0.9% SP2		C2 + 0.9% SP1 + 2% G1	
	C2 + 0.2% SP3		C2 + 0.2% SP2 + 2% G1	
	C2 + 0.5% SP3		C2 + 0.9% SP2 + 2% G1	
	C2 + 0.9% SP3		C2 + 0.2% SP3 + 2% G1	
	C2 + 0.2% SP4		C2 + 0.9% SP3 + 2% G1	
	C2 + 0.5% SP4		C2 + 0.2% SP4 + 2% G1	
	C2 + 0.9% SP4		C2 + 0.9% SP4 + 2% G1	
	C3 + 0.2% SP1		C2 + 0.2% SP1 + 6% G1	
	C3 + 0.5% SP1		C2 + 0.9% SP1 + 6% G1	
	C3 + 0.9% SP1		C2 + 0.2 SP2 + 6% G1	
	C3 + 0.2% SP2		C2 + 0.9% SP2 + 6% G1	
	C3 + 0.5% SP2		C2 + 0.2% SP3 + 6% G1	
	C3 + 0.9% SP2		C2 + 0.9% SP3 + 6% G1	
	C3 + 0.2% SP3		C2 + 0.2% SP4 + 6% G1	
	C3 + 0.5% SP3		C2 + 0.9% SP4 + 6% G1	

	C3 + 0.9% SP3		C3 + 0.2% SP1 + 2% G1	
	C3 + 0.2% SP4		C3 + 0.9% SP1 + 2% G1	
	C3 + 0.5% SP4		C3 + 0.2% SP2 + 2% G1	
	C3 + 0.9% SP4		C3 + 0.9% SP2 + 2% G1	
			C3 + 0.2% SP3 + 2% G1	
			C3 + 0.9% SP3 + 2% G1	
			C3 + 0.2% SP4 + 2% G1	
			C3 + 0.9% SP4 + 2% G1	
			C3 + 0.2% SP1 + 6% G1	
			C3 + 0.9% SP1 + 6% G1	
			C3 + 0.2 SP2 + 6% G1	
			C3 + 0.9% SP2 + 6% G1	
			C3 + 0.2% SP3 + 6% G1	
			C3 + 0.9% SP3 + 6% G1	
			C3 + 0.2% SP4 + 6% G1	
			C3 + 0.9% SP4 + 6% G1	

### 3.8. Conclusion

The materials used in this study are discussed and characterised in this chapter, while also considering the different tests conducted. The mixing-, as well as the testing procedure, are discussed and finally, a summary of the mixes used during this study is given. The results obtained during the testing procedure are shown and discussed in Chapter 4 and 5.

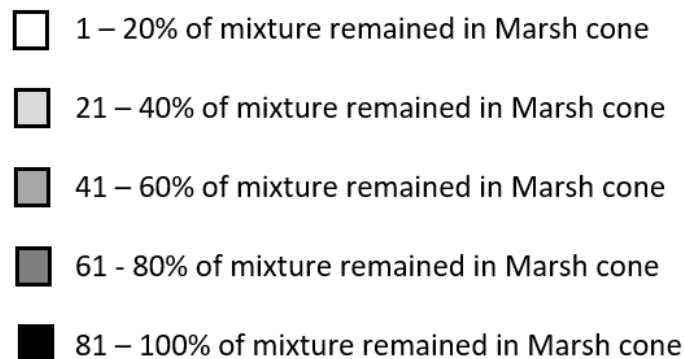
## 4. INDIVIDUAL RESULTS OF CLINKER, SUPERPLASTICISER AND SULPHATE

In this chapter, the results of the different tests are discussed and compared to identify possible compatibility issues. The numerical results for all tests conducted can be found in Appendix D.

During the Marsh cone testing, as mentioned in Chapter 3, not all mixes were able to flow freely through the Marsh cone, with some of the paste remaining in the cone when the continuous flow stopped. Different markers, as described as follows, were used to indicate the nature of the observed flow.

- Coloured dot; the cone emptied without a discontinuity in the flow stream
- Red triangle; segregation of the mixture occurred
- Square; paste remained in the cone, discontinuity in the flow stream

The squares, seen in Figure 4.1, further indicate the amount of mixture remaining in the Marsh cone at times; 0-, 20-, 40- and 60 minutes, while the flow time associated with these markers on a graph indicates the time of continuous flow measured for that certain mix



*Figure 4.1: Key to remainder of paste in Marsh cone after testing*

### 4.1. Clinker type

The results of the three different clinkers are compared and the results of the reference mixes are briefly reviewed to evaluate the repeatability of the results.

#### 4.1.1. Clinker compositions

The chemical compositions of the three different clinkers can be seen in Table 4.1.

Table 4.1: Composition of clinkers considered for this study

%	C1 -Dwaalboom	C2 - De Hoek	C3 - Slurry
SiO <sub>2</sub>	21.8	22.2	22.4
Al <sub>2</sub> O <sub>3</sub>	5.1	4	4.4
Fe <sub>2</sub> O <sub>3</sub>	3.3	2.8	3
Mn <sub>2</sub> O <sub>3</sub>	0.6	0.1	0.1
TiO <sub>2</sub>	0.3	0.3	0.5
CaO	66.5	67	66.8
MgO	2.9	1.2	1.5
P <sub>2</sub> O <sub>5</sub>	0.04	0.2	0.1
Cl	0.03	0.04	0.03
SO <sub>3</sub>	0.19	0.71	0.44
K <sub>2</sub> O	0.14	0.62	0.19
Na <sub>2</sub> O	0	0.2	0.04
FCaO (Free Lime)	1.6	1.7	2.5

The Bogue equations were used to calculate the percentages of C<sub>2</sub>S, C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF in the different clinkers, with the results shown in Table 4.2.

Table 4.2: Percentage of clinker phases

Bogue Calculation	C1 -Dwaalboom	C2 - De Hoek	C3 - Slurry
	[%]		
C <sub>3</sub> S	56.07	59.06	50.07
C <sub>2</sub> S	21.38	20.58	27.95
C <sub>3</sub> A	6.44	5.59	6.83
C <sub>4</sub> AF	11.93	8.88	9.74
Na <sub>2</sub> O <sub>eq</sub> (Total alkali)	0.13	0.56	0.17

The amount of the different clinker phases present in cement varies with both the purpose of the cement, as well as the type and quality of raw materials used during the production process. This

suggests that a relatively high content of a certain clinker phase in one type of cement could be considered as normal in a different type of cement. In this study, the high-, medium- and low content of the various phases are merely comparative, distinguishing between the different clinkers used. This attempt only aims at linking compatibility issues between calcium sulphate and superplasticiser to a specific clinker phase and not to suggest a specific level of clinker phases in cement will lead to a definite incompatibility.

Table 4.2 shows that C1, the Dwaalboom clinker, has the highest amount of  $C_4AF$  and an in-between, referred to as medium, amount of  $C_2S$ ,  $C_3S$  and  $C_3A$  and the lowest total alkali content. C2, the De Hoek clinker, has the highest  $C_3S$  content, and lowest  $C_2S$ ,  $C_3A$  and  $C_4AF$  content while also having the highest total alkali content. C3, the Slurry clinker, has the highest  $C_2S$  and  $C_3A$  content, with a medium  $C_4AF$  and lowest  $C_3S$  content, while also having a medium percentage of total alkali compared to the other clinkers.

#### 4.1.2. Mini slump

From the mini slump results seen in Figure 4.2, the results of the three reference mixes for each of the three clinkers can be compared.

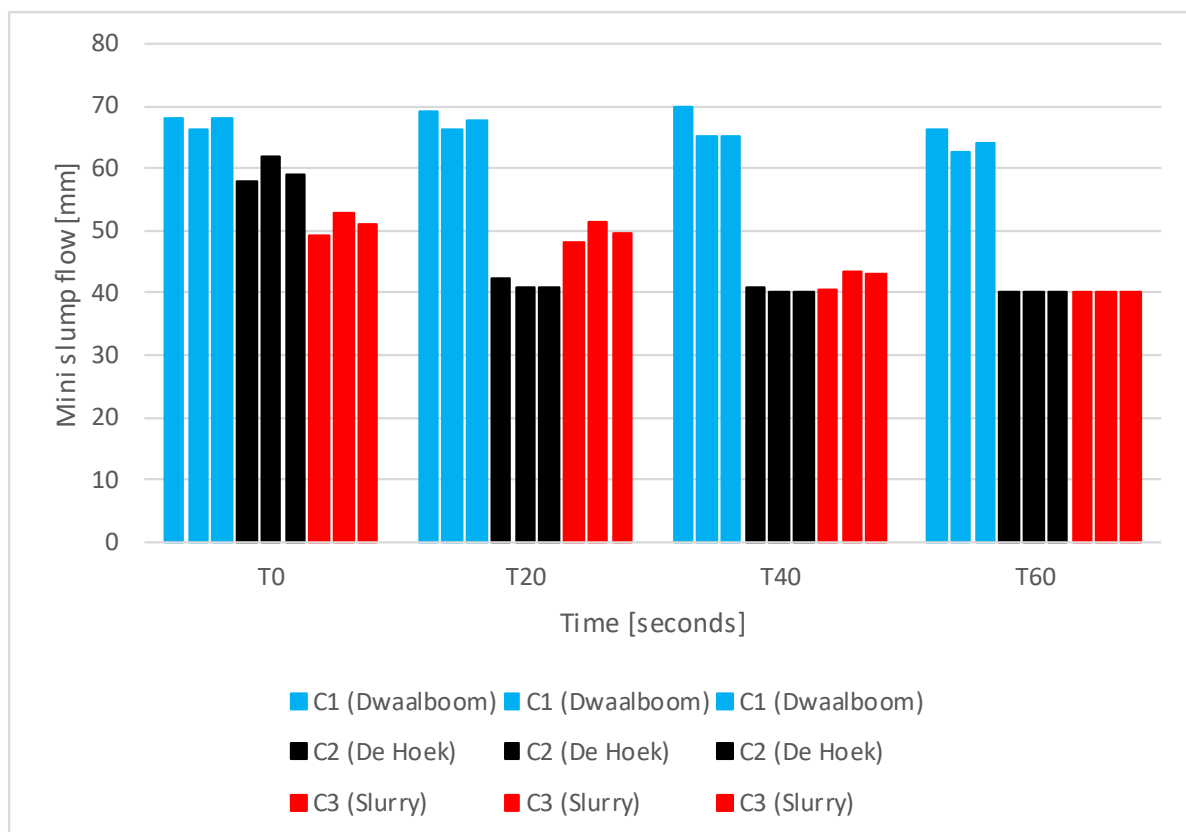


Figure 4.2: Mini slump test results for reference mixes of each clinker

It is found that for all three clinkers considered, similar results were obtained for the three mixes respectively, indicating the results can be repeated and is sufficient to be used in this study. The standard deviation for the various clinkers can be seen in Figure 4.3 when considering the mini slump test.

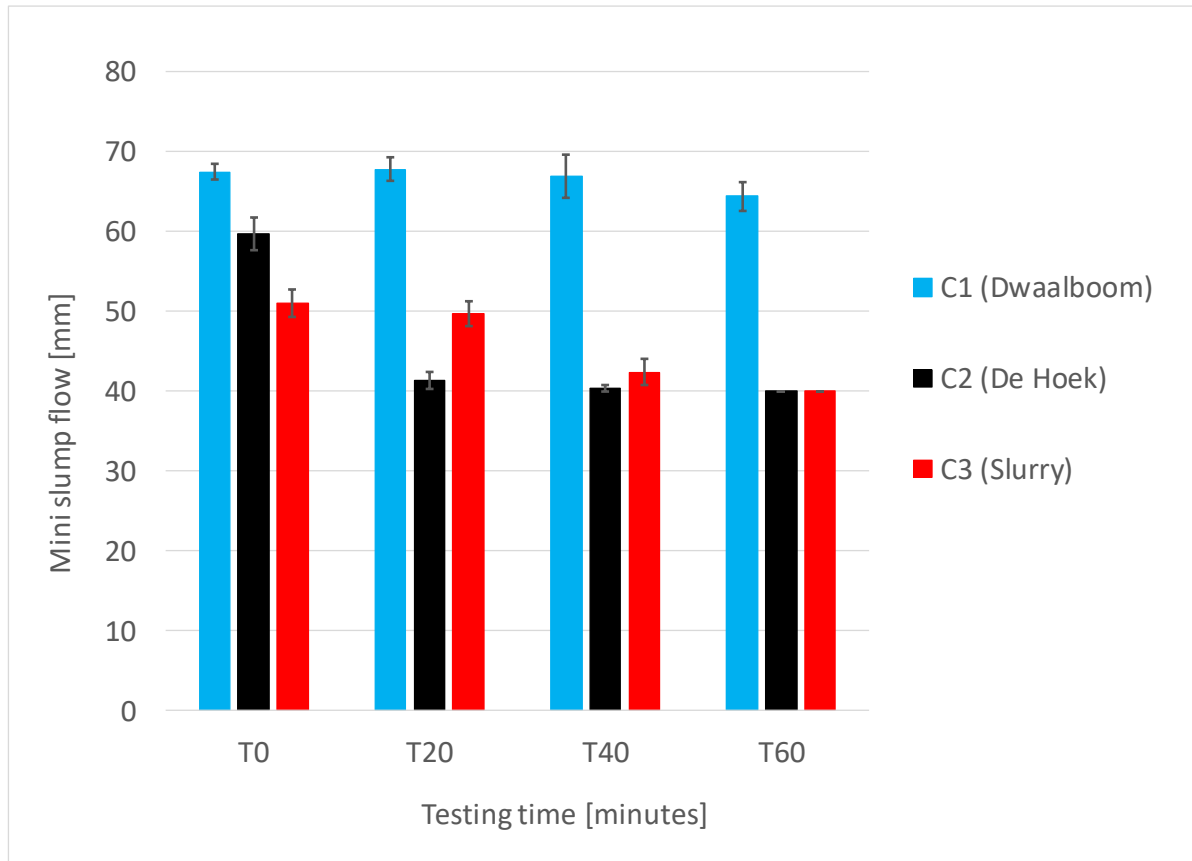


Figure 4.3: Mini slump test results for reference mixes with standard deviation

Figure 4.4 shows the average mini slump results of the three different reference mixes. In Figure 4.4, C1 has the highest initial slump flow, at 0 minutes, and C3 the lowest. The measured initial slump flow of C2 is roughly in between that of the other two clinkers.

Over time, C1 maintained a relatively constant slump flow, only decreasing slightly when reaching the end of the testing period at 60 minutes. C3 shows a steady decline in slump flow over time while for C2, a drastic decrease in slump flow occurred between testing times 0 minutes and 20 minutes, after which the slump flow stays relatively constant up to 60 minutes testing time.

These results, as seen in Figure 4.4, conforms with the findings of Dengwu et al. (2017) who found that cement with a high  $C_3A$  or alkali content, has a decreased workability. This is depicted in the



results with C2 having the highest alkali content and C3 having the highest  $C_3A$  content of the clinkers considered.

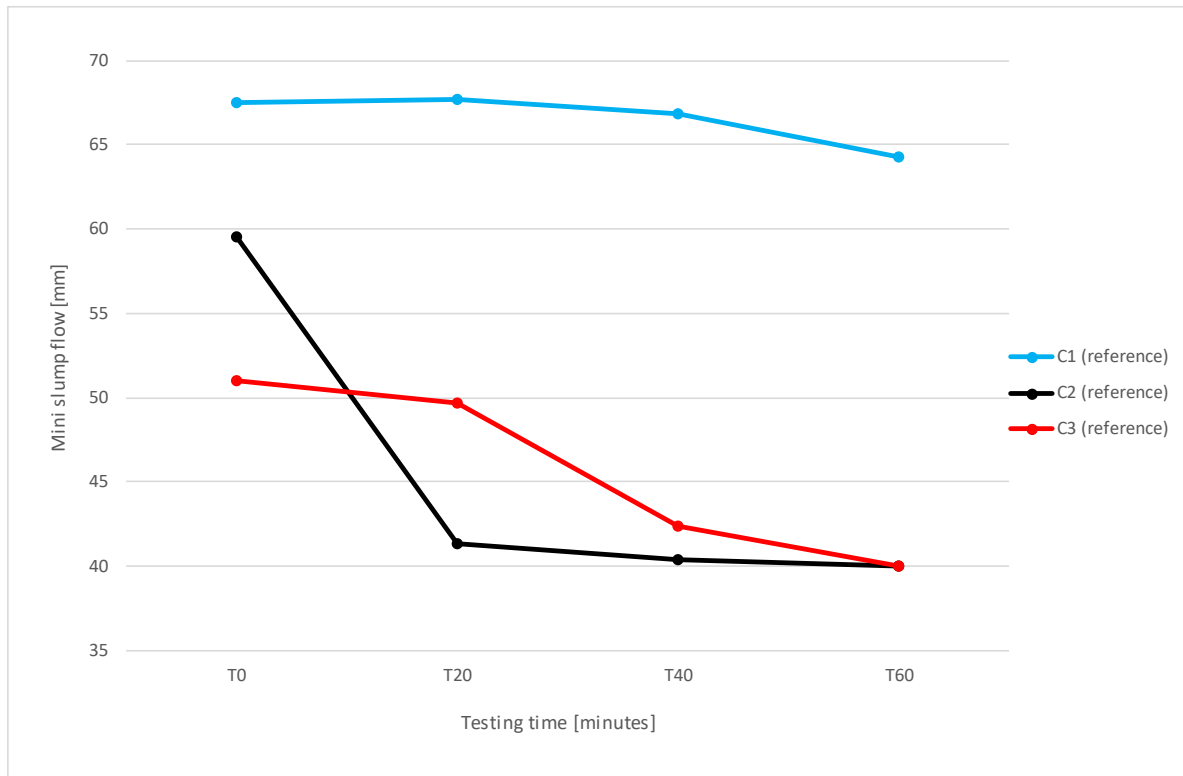


Figure 4.4: Mini slump results comparing reference mixes

The particle size distribution in Chapter 3 showed a similar trend for C1 and C3, with C2 having a slightly smaller average particle size than that of the other clinkers. It would, therefore, be expected that the similarity in flowability would be between C1 and C3, with C2 having a lower flowability due to the higher water demand associated with the smaller particle size – albeit only slightly. However, as seen in Figure 4.4, C1 was found to have a much higher flowability both initially and throughout the testing period, compared to C2 and C3. This suggests that the high  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content of C1 is more efficient in increasing the flowability of the paste, governing the effect of the particle size on the flowability of the cement mix.

#### 4.1.3. Marsh cone

For the Marsh cone test, the results for the three different references were found to be similar for each of the respective clinkers, as seen in Figure 4.5.

For C1, the Marsh cone resulted in a clean flow for testing times 0 - and 20 minutes, while for testing time 40 minutes; 1%, 3% and 1% of the concrete mix remained in the Marsh cone after testing while for time 60 minutes, the values increased to 8%, 10% and 7%. C2 showed 24%, 30% and 28% of the respective mixes remaining in the cone after testing at time 0 minutes, while only a few drops were observed at the other testing times considered. At time 0 minutes, 80%, 73% and 60% of the reference paste containing C3 were found remaining in the cone, with 93%, 92% and 80% remaining respectively at time 20 minutes. At time 40 minutes, 97%, 96% and 95% of the mixture remained in the Marsh cone after testing with only a few drops observed at time 60 minutes.

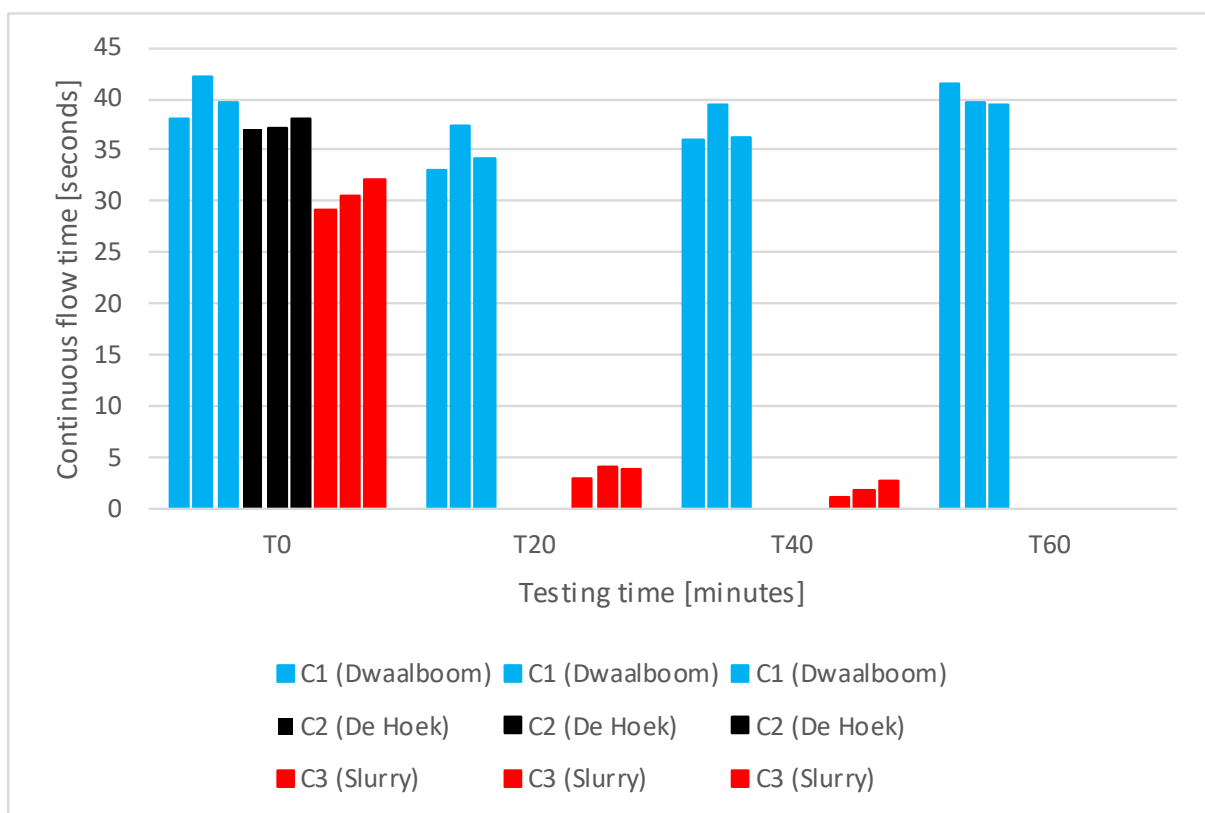


Figure 4.5: Marsh cone test results for reference mixes of each clinker

For the Marsh cone test, the standard deviation in the reference mix results can be seen in Figure 4.6.

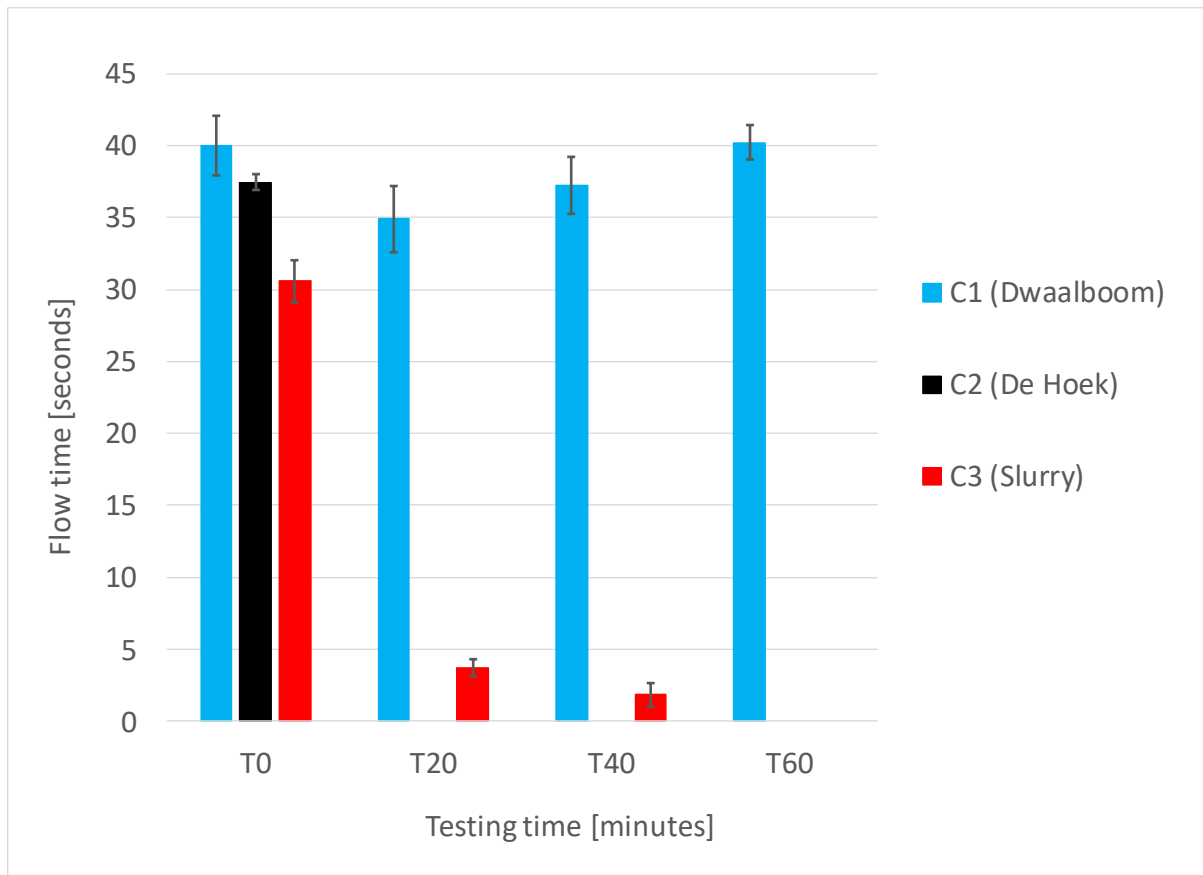


Figure 4.6: Marsh cone test results for reference mixes with standard deviation

Figure 4.7 shows the average Marsh cone result of the three reference mixes. C1 shows a slight decrease in flow time, which means the flowability of the mix increased initially, but over time, after 40 minutes and 60 minutes, the flowability of the paste was not enough to ensure a continuous flow out of the Marsh cone, with some of the paste (2% and 6% respectively) remaining in the flow cone. With no superplasticiser, a sticky paste resulted for the reference mix containing C2, with a high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content leaving behind around 27% of the mix inside the Marsh cone after the continuous-flow stream stopped at 37 seconds. For C3 around 71% of the mixture remained in the Marsh cone after flow stopped at 30 seconds when tested initially. As testing proceeded more of the mix remained in the cone, while only a few drops exiting the cone at the end of the testing period.

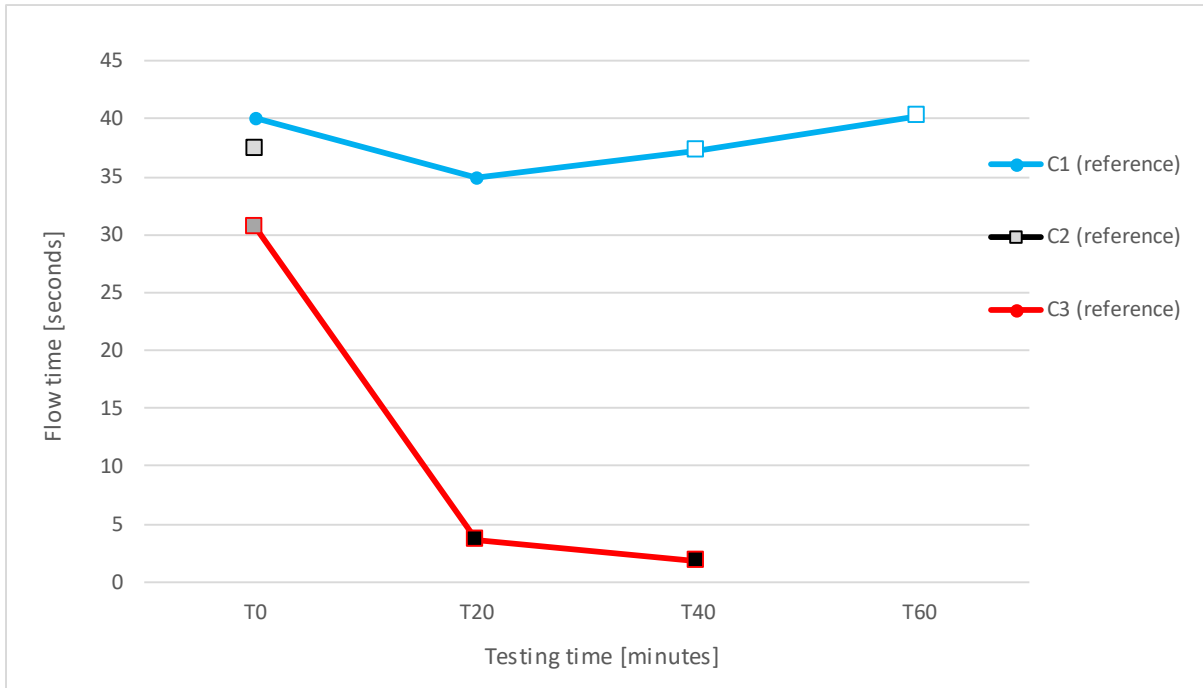


Figure 4.7: Marsh cone results comparing reference mixes

#### 4.1.4. Setting time

Again, the three different results for the setting time of the three clinkers respectively obtained similar results, as seen in Figure 4.8, and can, therefore, be considered as suitable for this study.

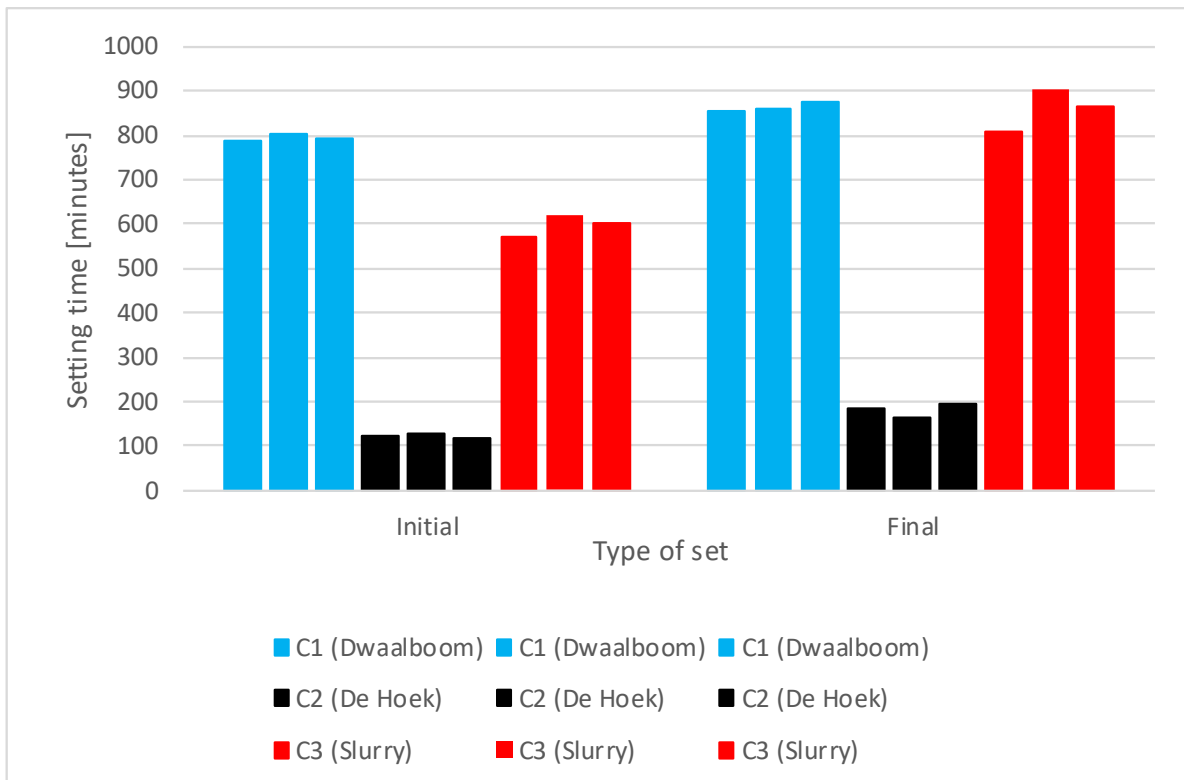


Figure 4.8: Initial and final setting times for reference mixes of each clinker

The standard deviation on the setting times for each of the three different clinkers can be seen in Figure 4.9.

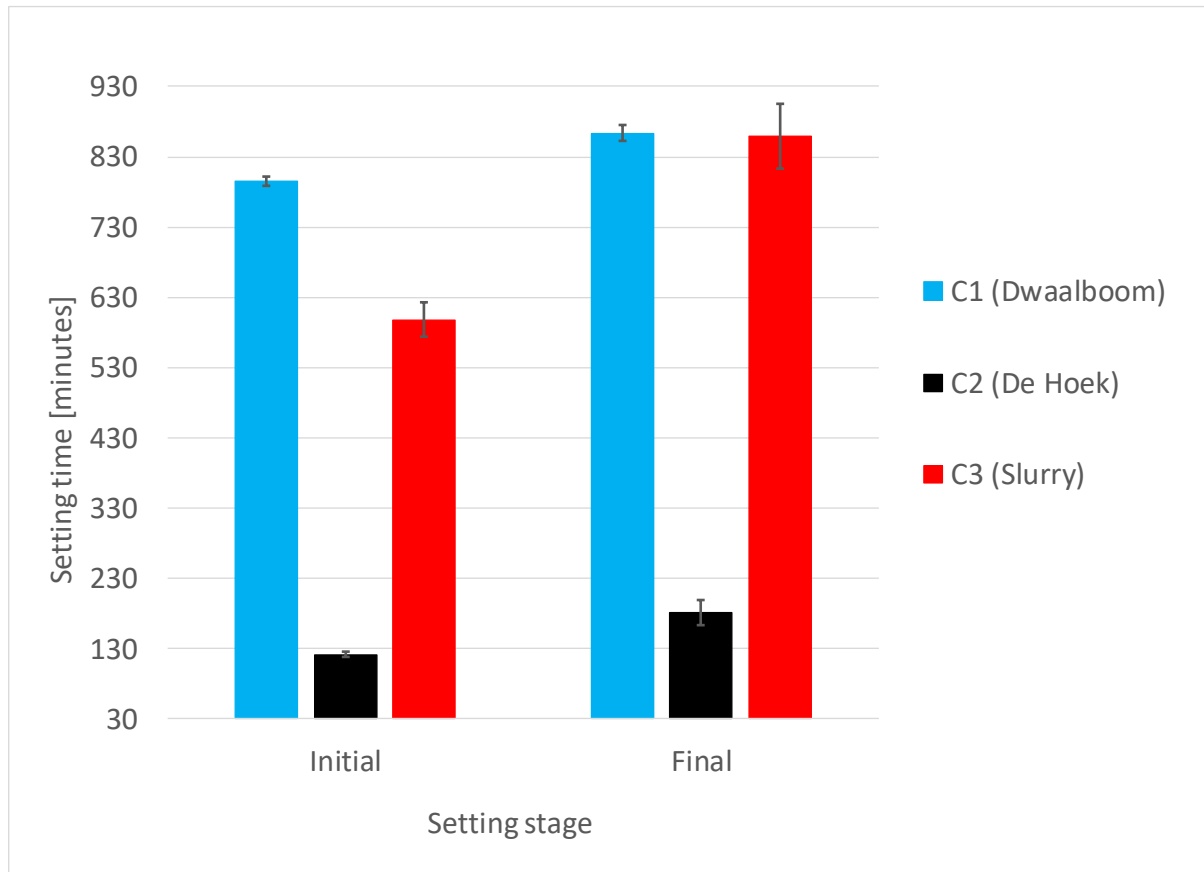


Figure 4.9: Setting time results for reference mixes with standard deviation

Figure 4.10 shows the effect of the different clinkers on the average setting times. The results show that C2 has a much lower initial and final setting time at around 2 and 3 hours respectively, compared to the other two clinkers, which show setting times in excess of 10 hours.

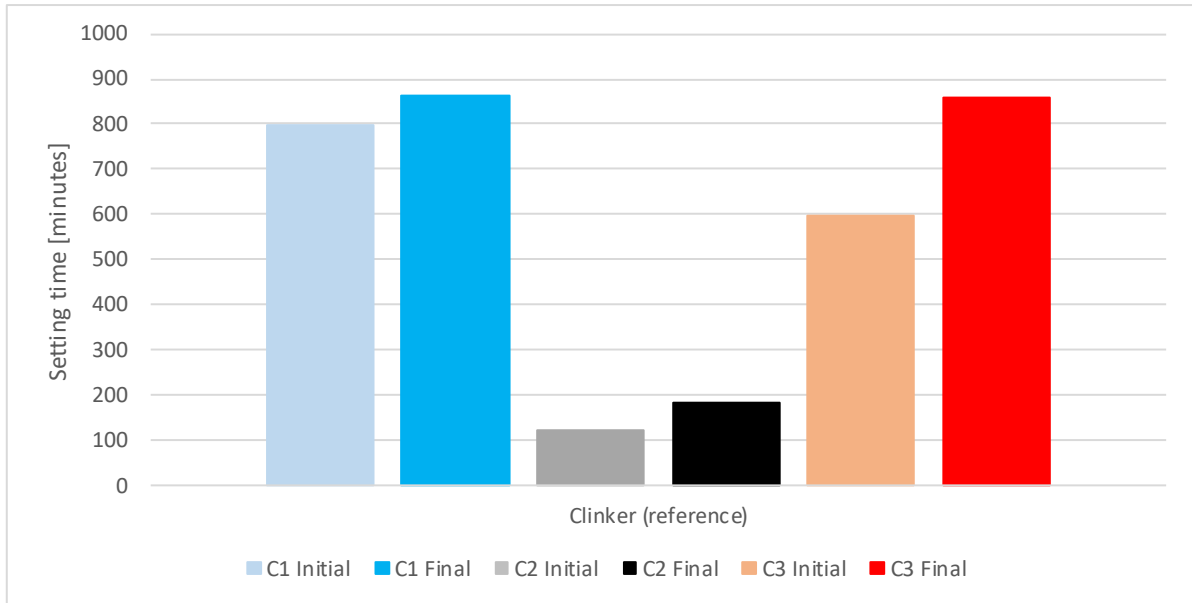


Figure 4.10: Setting time results comparing reference mixes

#### 4.1.5. Strength

Both the 2-day and 7-day results for the strength tests for the three different clinkers was proven to be repeatable as seen in Figure 4.11.

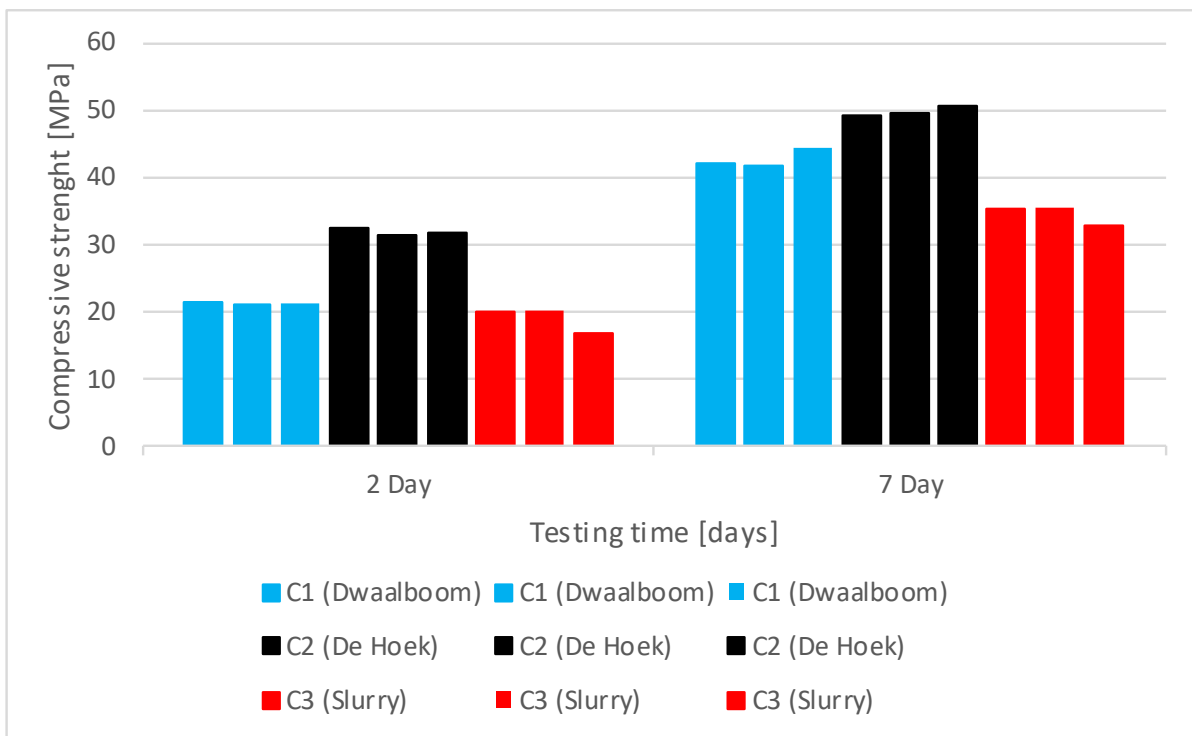


Figure 4.11: Strength test results for reference mixes of each clinker

Figure 4.12 shows the standard deviation for each of the different mixes when considering the reference mixes.

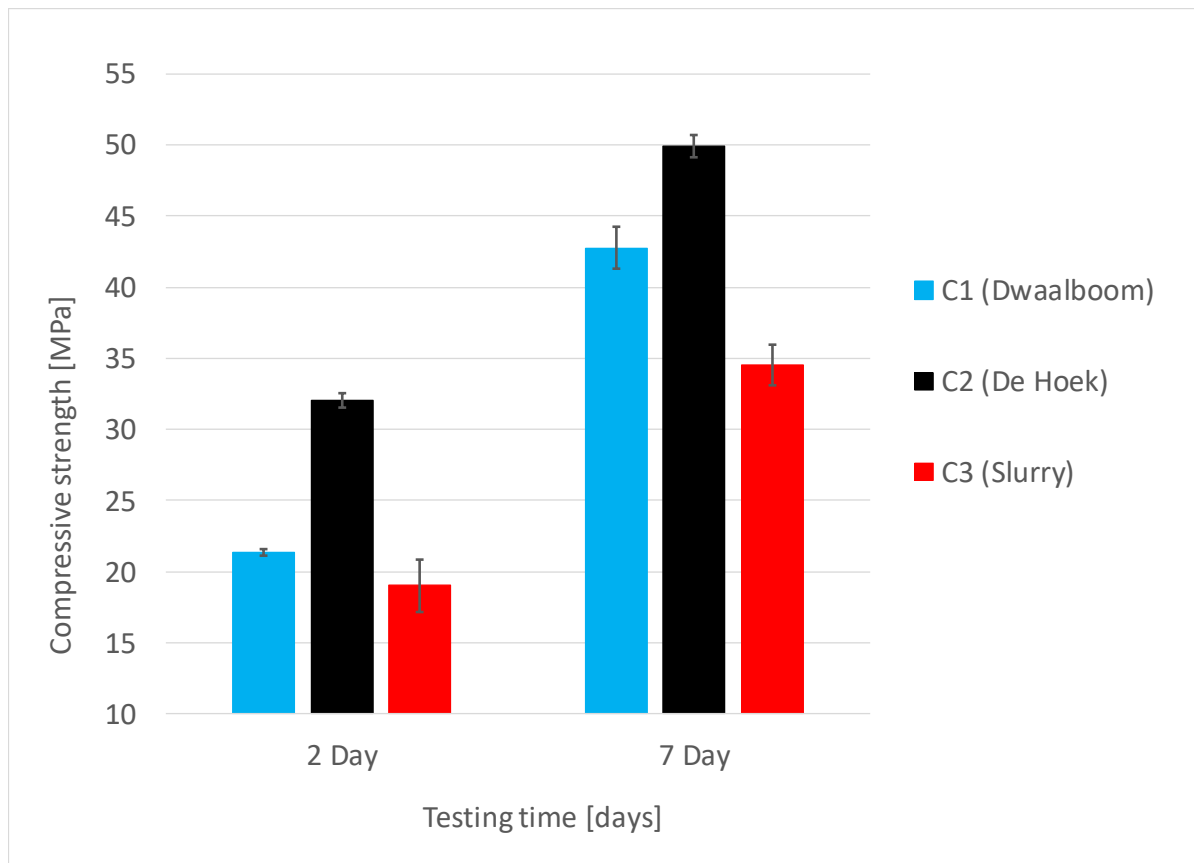


Figure 4.12: Strength test results for reference mixes with standard deviation

Figure 4.13 shows the effect the different clinkers on the average compressive strength of the reference mixes. For the reference mixes, C1 and C3 show a similar 2-day compression strength, while C1 shows a much higher 7-day compressive strength compared to C3. C2 has a higher compressive strength at both the 2- and 7-day testing times than the other clinkers.



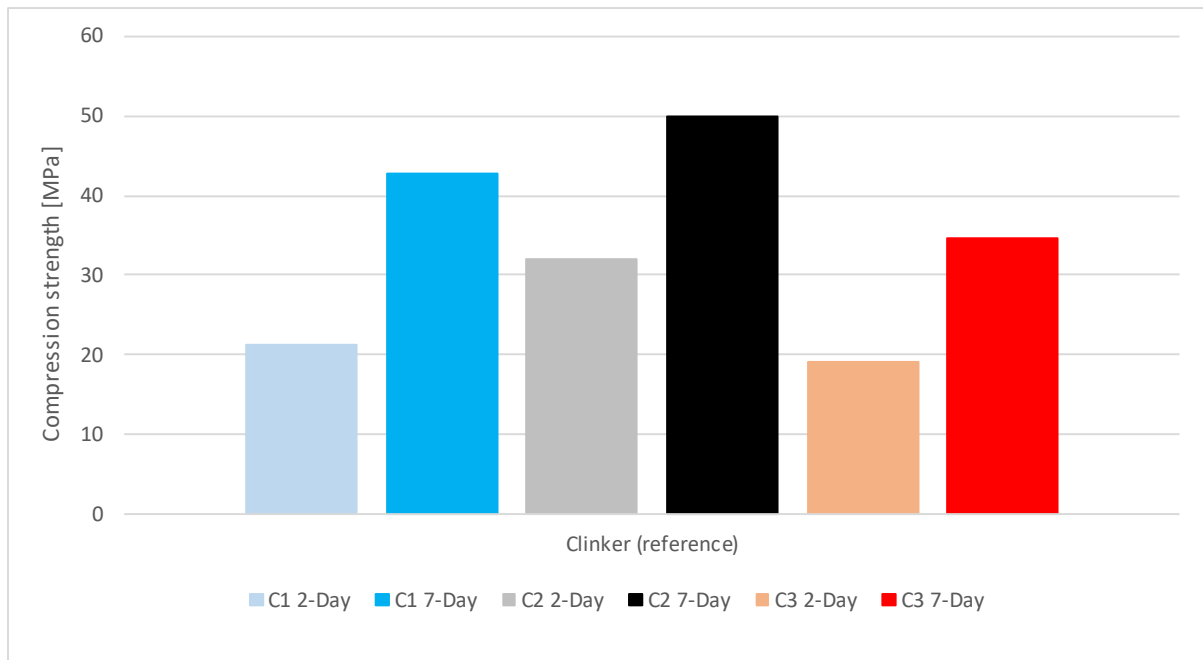


Figure 4.13: Strength test results comparing reference mixes

#### 4.1.6. Repeatability of results

From the results of the reference mixes, a good repeatability was found, with all the graphs showing one standard deviation as a measure of variability. The standard deviation for all three clinkers tested is small, indicating that the tests showed good repeatability.

#### 4.1.7. Concluding summary

Since all three reference mixes were found to deliver repeatable results for all tests considered, it can be assumed that these clinkers are suitable for research testing.

Both the mini slump and the Marsh cone test results indicate a constant, better flowability for C1, without any additions, compared to C2 and C3. While both tests also indicate similar results for C2 and C3 respectively, suggesting that C2 has an increased initial flowability compared to C3, but that this increase only lasts for a short period as a drastic decrease in flowability is noted for C2 soon after the initial testing, while the flowability gradually decreases for C3. Although C2 show much shorter setting times than the other clinkers considered, which also explains the higher 2- and 7-day compression strength reached for C2 compared to the other clinkers. This can also be explained by the higher  $C_3S$  content of C2 compared to the other clinker, which is known to hydrate and contribute to strength during the early stages. Another interesting observation that can be made is that none of the clinkers showed flash setting even though no gypsum was added as done for any conventional cement to prevent flash setting.

From the mini slump test results, it was concluded that the chemical composition of the different clinkers governed the particle size distribution when considering the flowability of the mix. The results obtained in this study is therefore expected to be able to give an insight on the effect the interactions between calcium sulphate, superplasticisers and the various clinker phases have on the flowability of the mix, without the particle size of the clinker obscuring the results.

## 4.2. Superplasticiser type

In this section, the effect of the different superplasticiser at various dosages, in addition to the water, in combination with the three clinker types without any added gypsum is discussed.

### 4.2.1. Superplasticiser composition

As mentioned, when discussing the superplasticiser used in this study, three PCE based superplasticisers were considered;

- Superplasticiser 1 (SP1); a general PCE based superplasticiser.
- Superplasticiser 2 (SP2); a PCE based superplasticiser designed to be compatible with Western Cape cements.
- Superplasticiser 3 (SP3); a PCE designed to be more compatible with low alkali cements.

As mentioned, no information regarding the chemical composition of these respective PCEs could be obtained, which includes details about the different chain lengths and the molecular weights.

A fourth superplasticiser, SP4 which is a naphthalene-based product, was also used for testing.

### 4.2.2. Mini slump results

For SP1, a more general PCE superplasticiser, the results show that the measured slump flow increased as the dosage increased for all three types of clinker, as seen in Figure 4.14. The addition of superplasticiser increased the slump flow of the clinker proportional to that of the reference mixes, the graphs have the same shape or trend as the reference mixes just at a greater slump flow. Both C1 and C3 show a steady decrease in slump flow as the time of testing increases for all superplasticiser dosages, with C3 showing a slightly larger decrease with time compared to C1. This indicates that for C1 and C3, there is a gradual, almost linear, decrease in followability with time.

For C2, also seen in Figure 4.14, with 0%, 0.2% and 0.5% dosage of SP1, the initial slump flow at 0 minutes is much higher than that measured after 20-, 40- and 60-minutes. The slump flow results from 20 to 60 minutes are nearly similar, especially for the 0% and 0.2% dosages. With the dosage of 0.9% of superplasticiser, this significant decrease in slump flow did not occur between the 0- and 20-minute testing mark as for the rest of the tests and shifted to between the 20- and 40-minute tests.

The results indicate that the SP1 increases the slump flow of a mix as the dosage thereof increases but then loses its effectiveness, or gets worked out faster, for a clinker with a high  $C_3S$ , low  $C_2S$  content i.e. C2, which show a significant loss in flowability at a certain time. For the lower dosages of SP1, this loss occurred within 20 minutes, while at higher dosages of SP1 this only occurred within 40 minutes. This suggests that for C2, a higher dosage of SP1 is initially not that effective, but that effect of the superplasticiser with time is sustained for longer compared to lower dosages.

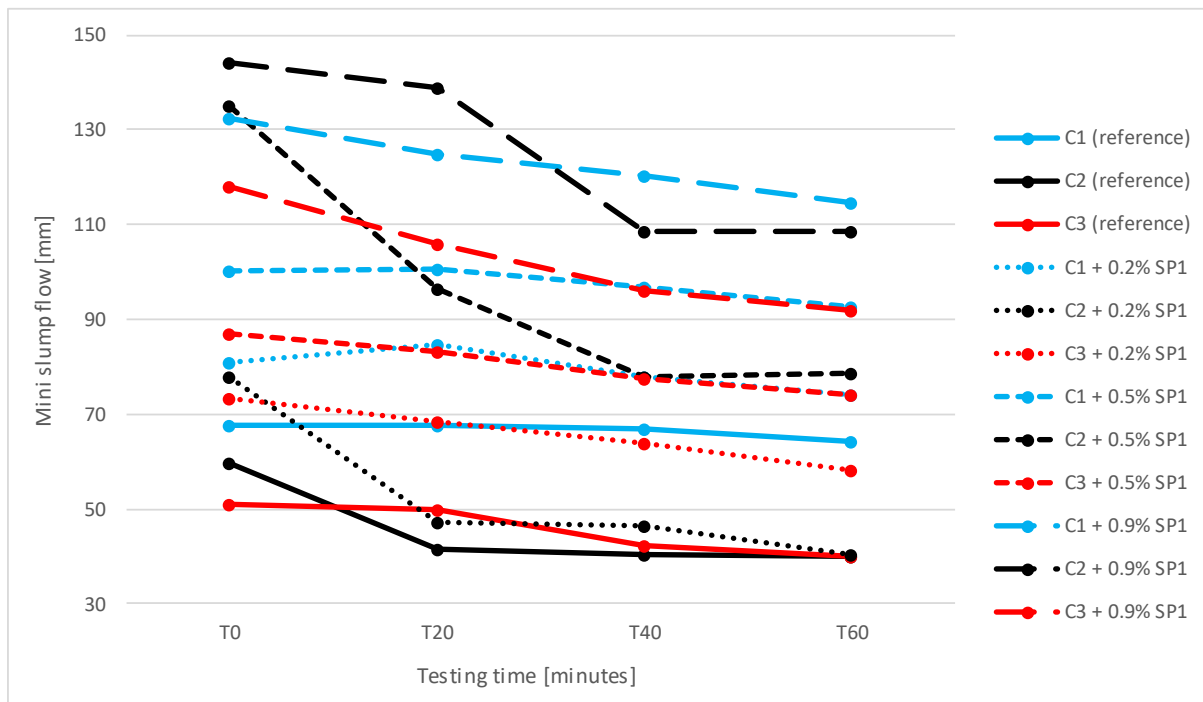


Figure 4.14: Mini slump results for different clinkers in combination with SP1

With the addition of SP2, a PCE based superplasticiser designed to be compatible with Western Cape cements – C2 in this case, the results obtained are shown in Figure 4.15 and is found to be similar to that of SP1 in Figure 4.14.

For all three clinkers, SP2 showed an increase in slump flow at time 0 minutes, proportional to the increase in dosage. C1 resulted in a rather small increase in flowability between the 0.2% and 0.5% dosages, compared to the other increments. Over time, a similar trend was observed for the 0.2%, 0.5% and the 0.9% dosage, with the result obtained at 20 minutes being similar to that of the result measured at 0 minute testing time, where after a similar slight decrease in flowability is noted as for the other dosages.

C2 shows a similar increase in flowability to that of C1 when compared to the reference mix, while again, a larger increment in the increased slump flow is measured between the 0.5% and 0.9% dosages when compared to that of the other dosages. A gradual decrease in flowability was observed during the period of testing, again similarly to C1, without any notable deviations.

C2, as seen in Figure 4.15, show that while also having an increased slump flow at 0-minute testing time for all the dosages considered, the biggest increase happened between the 0.2% and 0.5% dosages, other than for C1 and C3. Similar to C1 and C2, the shape of the graph showing the slump loss over time is similar to that of the reference mix, only shifted upwards on the axis, for both the 0.2% and 0.5% dosages. For the 0.9% addition the gradient of the graph changed to show the biggest loss of workability to happen between testing times 20 minutes and 40 minutes, instead of between 0- and 20 minutes, as for the 0.2% and 0.5% additions, suggesting the higher dosage takes longer to lose its effectiveness.

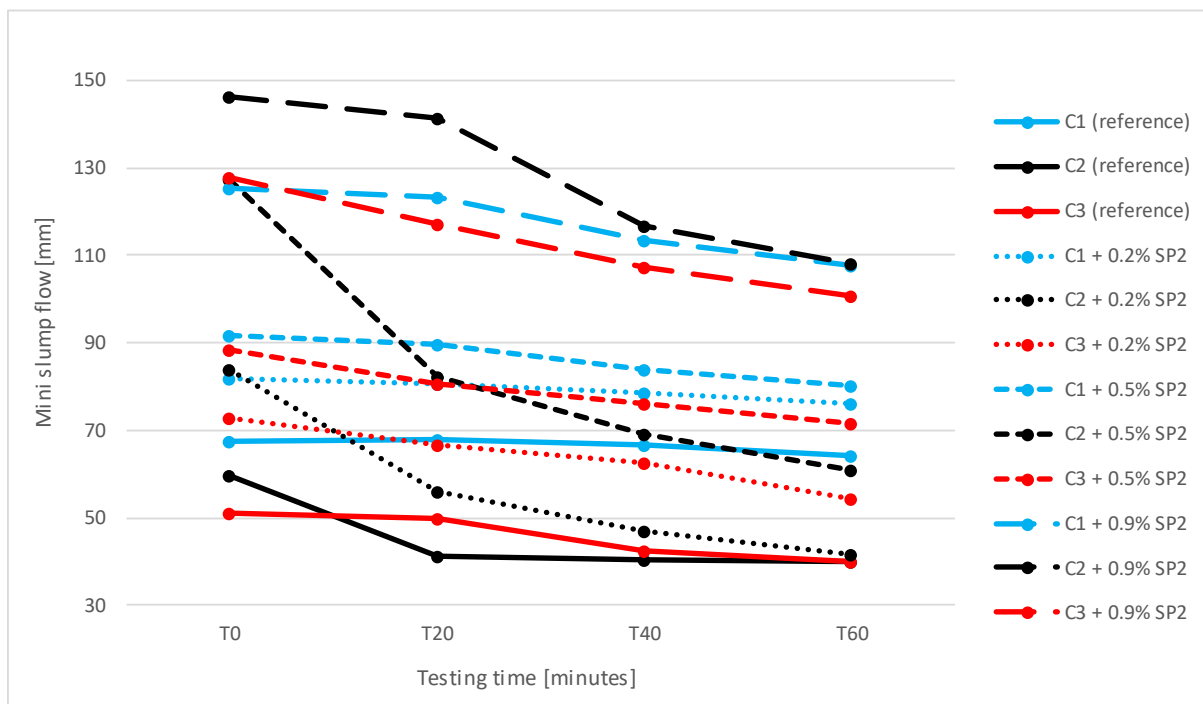


Figure 4.15: Mini slump results for different clinkers in combination with SP2

The results of the tests containing SP3; a PCE designed to be more compatible with low alkali cements, can be seen in Figure 4.16, again showing similarity to Figures 4.14 and 4.15.

With the dosage of 0.2% superplasticiser, C3 showed the biggest increase in slump flow, while the slump flow of C1 and C2 merely increased while maintaining the same trend as that of the reference

mixes. However, the initial increase in slump flow of C2 at 0.2% dosage is drastically bigger than that of C1 – which has a medium C<sub>3</sub>S, C<sub>2</sub>S and C<sub>3</sub>A, and high C<sub>4</sub>AF content.

With the dosage of 0.5% SP3, C1 again showed the lowest increase in flowability, followed by C3 and then C2, which showed to have the biggest increase in flowability at this dosage. All three clinkers showed a similar trend over time at this addition than as that of the reference mix as well as the 0.2% dosage, with the slump flow being fairly constant for C1 and slightly decreasing for C3, while C2 showed a rapid loss in flowability between the 0 minute and 20 minute testing times, after which the slump loss gradient decreases over time.

With the highest dosage of 0.9% superplasticiser, a similar increase in slump flow was observed for C1 and C3, while at this dosage, C2 showed the lowest increase in slump flow from the previous dosage of 0.5%. C2 shows a constant decrease in slump flow from the start of testing up until the testing at 40 minutes, whereafter the slump flow loss started to stabilise, unlike C1 and C3 which showed fairly constant result over the testing period.

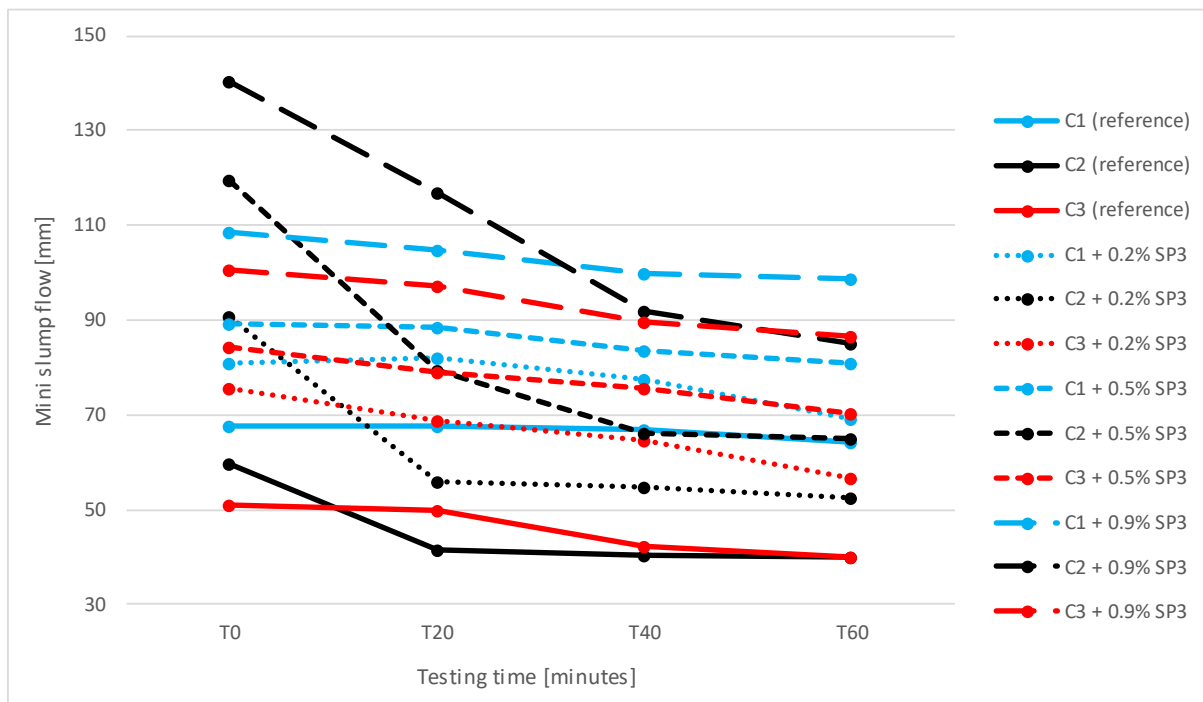


Figure 4.16: Mini slump results for different clinkers in combination with SP3

SP4; a naphthalene-based product, showed the lowest overall increase in slump flow throughout the tests, as seen in Figure 4.17. This conforms to the statement made by Biggs et al. (2010), that a higher dosage SNF based superplasticiser is needed than that of a PCE based superplasticiser, to achieve the

same results. Similarly, this finding is supported by Coppola et al. (2010), who suggested SNF based superplasticisers to be less efficient in water reduction than PCE based superplasticisers.

C1 resulted in a similar slump flow for all three dosages considered, with all three these results having a slump flow less than that of the reference mix. This indicates how this superplasticiser has a negative effect when used in combination with C1, which has a low  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content. The slump flow of the mixes containing C1 was found to be constant over the testing period, with only the 0.2% and 0.5% dosages showing a slight decrease in the flowability at time = 40 minutes.

C2 showed a slight increase in the 0-minute slump flow with the dosage of 0.2% SP4 but showed the same slump flow than the reference mix at the other testing times, which could indicate the superplasticiser is no longer effective in the period between 0 and 20 minutes. With a 0.5% dosage, an increase in slump flow was observed similar to that of the PCEs, however, over time, this slump flow decreased rapidly to find a result at the last time of testing to be the same as that of the reference mix. With 0.9% dosage, an increase in slump flow was found for all times of testing, although the slump flow still decreased with time, it was much higher than the reference mix, indicating that although the superplasticiser decreases in effectiveness over time, the dosage was high enough to overcome the mix's tendency to revert to the reference results.

For C3, Figure 4.17 show roughly the same slump flows were achieved with the dosage of 0.2% and 0.5% superplasticiser as for the reference mix. Only at 0.9% superplasticiser could a distinctive improvement in slump flow be observed however, it was still lower than with a dosage of 0.2% of any of the PCE type superplasticisers.

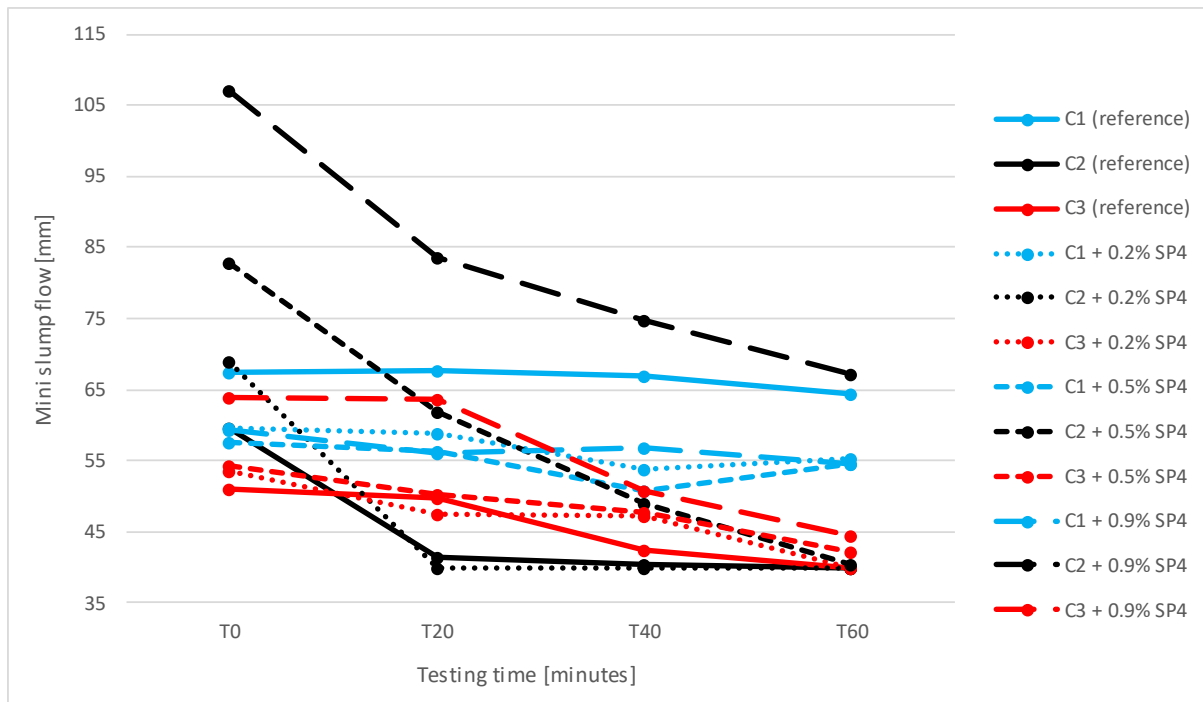


Figure 4.17: Mini slump results for different clinkers in combination with SP4

These results, summarised in Section 4.2.2, confirm the study of Jayasree et al. (2008) who found that the mini slump flow measurement increased as the dosage of superplasticiser is increased.

#### 4.2.3. Marsh Cone

With the dosage of 0.2% SP1 as shown in Figure 4.18, the Marsh cone emptied for all four of the testing times. The shape of the curve is similar to that of the reference mix with the flow time decreasing after the initial test but then increases again over time. With the dosage of 0.5% and 0.9% superplasticiser, a similar decrease in flow time can be observed, indicating that the extra 0.4% dosage did not have as big of an impact on the flowability of the paste than the 0.3% added to reach the 0.5% dosage from 0.2%.

Initially, a good flow time of 30 seconds was observed when 0.2% superplasticiser was added, however, as time progressed, the flow time decreased significantly with large amounts of paste remaining in the cone, with only a few drops present at the testing time of 60 minutes. For both the 0.5% and 0.9% superplasticiser dosages the mixtures segregated at the 0 minute testing time but after further mixing, the segregation stopped, leaving these two mixes to have identical results as time progressed.

With the dosage of 0.2% SP1, as seen in Figure 4.18, a similar initial flow time was measured than that of the reference mix however, all of the paste passed through the cone. The flow time increased over



time indicating the mixture becoming less flowable where, after a testing time of 40 minutes, the paste seems to have increased in flowability again. When adding 0.5% superplasticiser to the mix improvement in flowability resulted, decreasing over time, while for the 0.9% dosage the biggest increase in flowability is noted, staying fairly constant over the testing period.

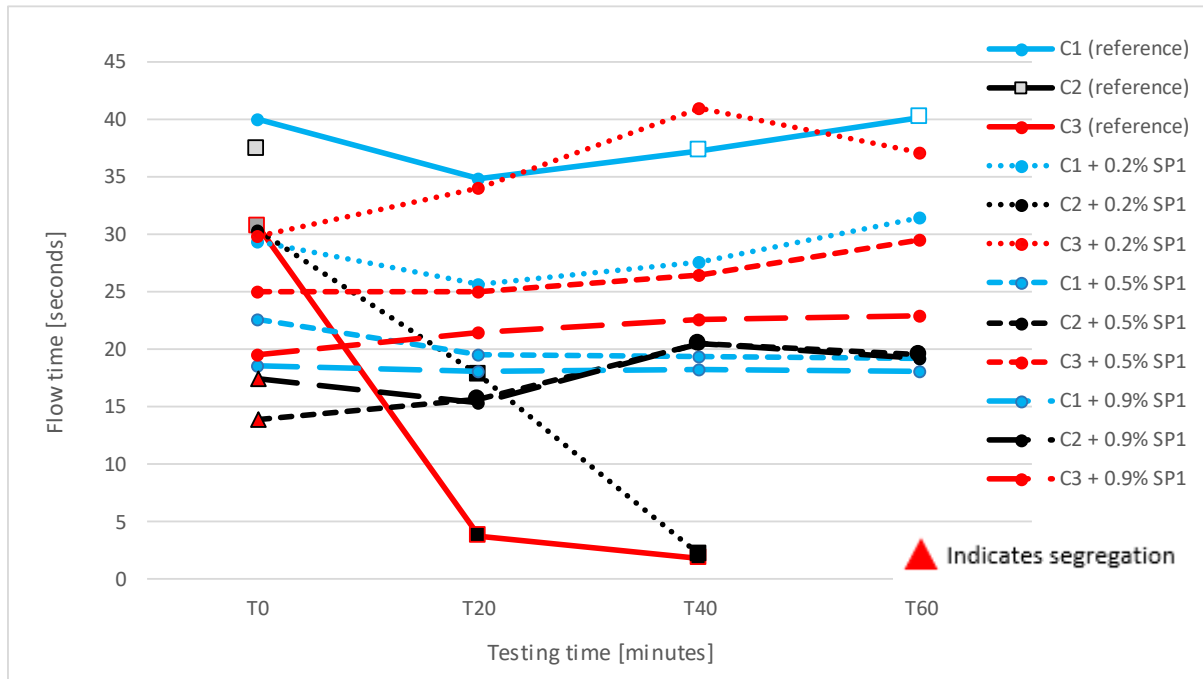


Figure 4.18: Marsh cone results for different clinkers in combination with SP1

When considering the results of SP2 as shown in Figure 4.19, C1 with high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content, the dosage of 0.2% and 0.5% superplasticiser delivered similar results, however, at 40- and 60-minutes, the continuous flow stopped for the 0.2% dosage suggesting that the lower dosage worked out sooner than that of the 0.5% dosage. A greater increase in flowability is noted for the 0.9% superplasticiser dosage, while it also maintained a constant flow rate.

Compared to the reference mix for C2, which stopped flowing with about 27% of the mix remaining in the Marsh cone after testing, a complete flow time of 21 seconds occurred when adding 0.2% superplasticiser. After the initial testing, this dosage decreases in effectiveness as the flow times decreased with time leaving behind 87% and 94% of the paste in the cone respectively, while only a few drops were observed at 60 minutes. With the 0.5% dosage, an increase in the flowability, as well as segregation, was observed at the 0-minute testing time. As the testing proceeded, the segregation stopped, and the flow time of the mix increased rapidly. The faster flow time for this superplasticiser

was observed with a dosage of 0.9% of SP2 to the C2 mix. Segregation occurred at both the 0-minute testing time as well as the testing time of 60 minutes however, throughout the duration of the testing procedure, a constant flow time occurred.

For C3, a similar result is shown for the dosage of 0.2% of SP2 to that of SP1, with the flow time increasing over time and then decreasing again after 40 minutes of testing. Similar results to that of SP1 is again shown for the 0.5% and 0.9% SP2 dosage, however, unlike when using SP1, the 0.9% dosage of SP2 caused segregation at the initial testing time.

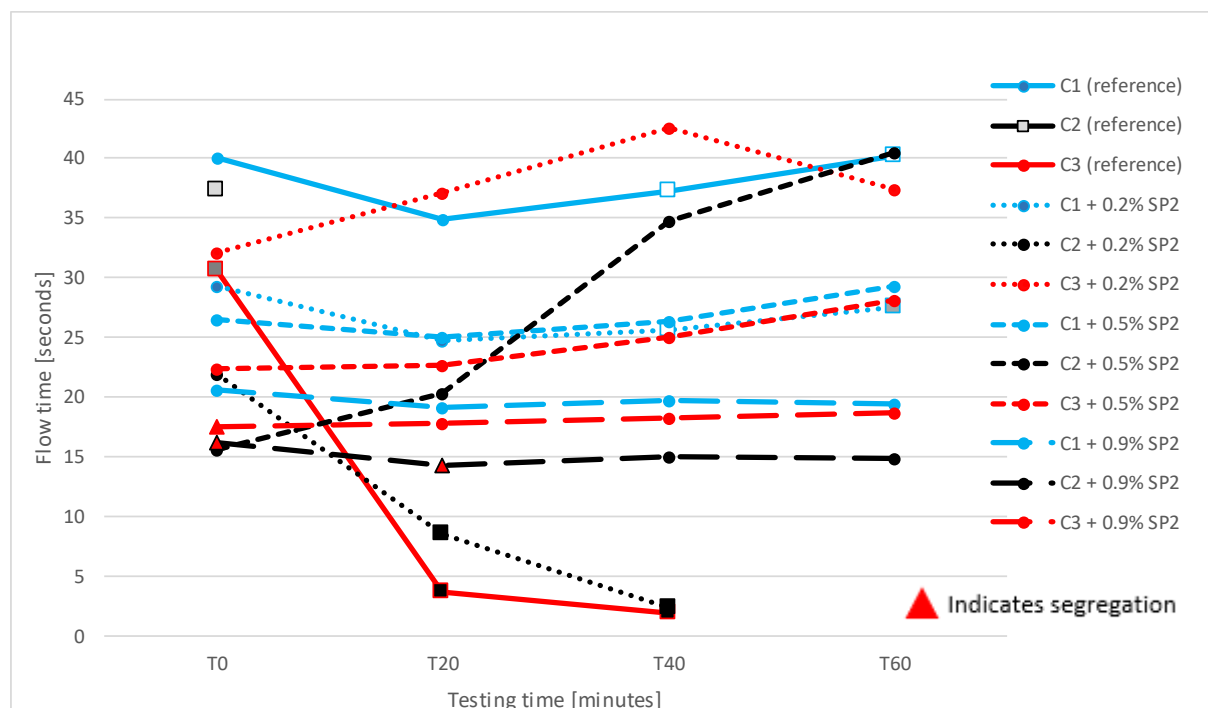


Figure 4.19: Marsh cone results for different clinkers in combination with SP2

With the addition of SP3 as shown in Figure 4.20, C1 shows that the improved flowability at T0 decreases much faster over time with the dosage of 0.2% SP3 than for SP1 and SP2. While similar improvements in flowability were obtained for the 0.5% and 0.9% dosages to that of the SP2. The 0.9% dosage was found to have, similar to that of SP2, the biggest influence in the higher flowability over time, while the 0.5% dosage, while also improving the flowability of the mix, loses some of its effectiveness as the flow time increased slightly over the duration of the testing procedure.

Figure 4.20 shows when adding 0.2% SP3 to the C2 mix, a significant increase in the initial flowability is shown, however, at testing time of 20 minutes, this increase was neutralised resulting in a flow time similar to that of the reference mix, also leaving behind approximately 12% of the paste remaining in

the cone. Over time, barely any flow time was measured for this mix, as it was too sticky resulting in most of the paste remaining in the Marsh cone. This could imply that the 0.2% superplasticiser dosage worked out during the 20-minute mixing time after the initial testing. When adding the 0.5% dosage, a similar increase in the initial flowability occurred than with the 0.2% dosage. The flow time of this mix steadily decreased at first where after a huge loss in flowability resulted. After an hour of mixing the paste became too sticky to empty from the cone, leaving about 5% remaining against the sides of the Marsh cone. With the dosage of 0.9% of this superplasticiser, a flow time similar to that of the other two addition mixes was found, however, segregation did occur at this high dosage. Over time the segregation of the mixture ceased while maintaining a similar flow time throughout the testing procedure.

C3 with high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  contents showed an increase in flow time with the dosage of 0.2% SP3, clearing the cone unlike when considering the reference mix. Over time, the flowability of the mixture decreased significantly with the paste managing to flow through the cone at testing time of 20 minutes but not clearing the Marsh cone at testing times that followed. The 0.5% and 0.9% dosages decreased the flow time by 10 and 14 seconds respectively. The 0.9% dosage maintained the increased flowability over time but for the 0.5% dosage, the flowability steadily decreased over the testing period.

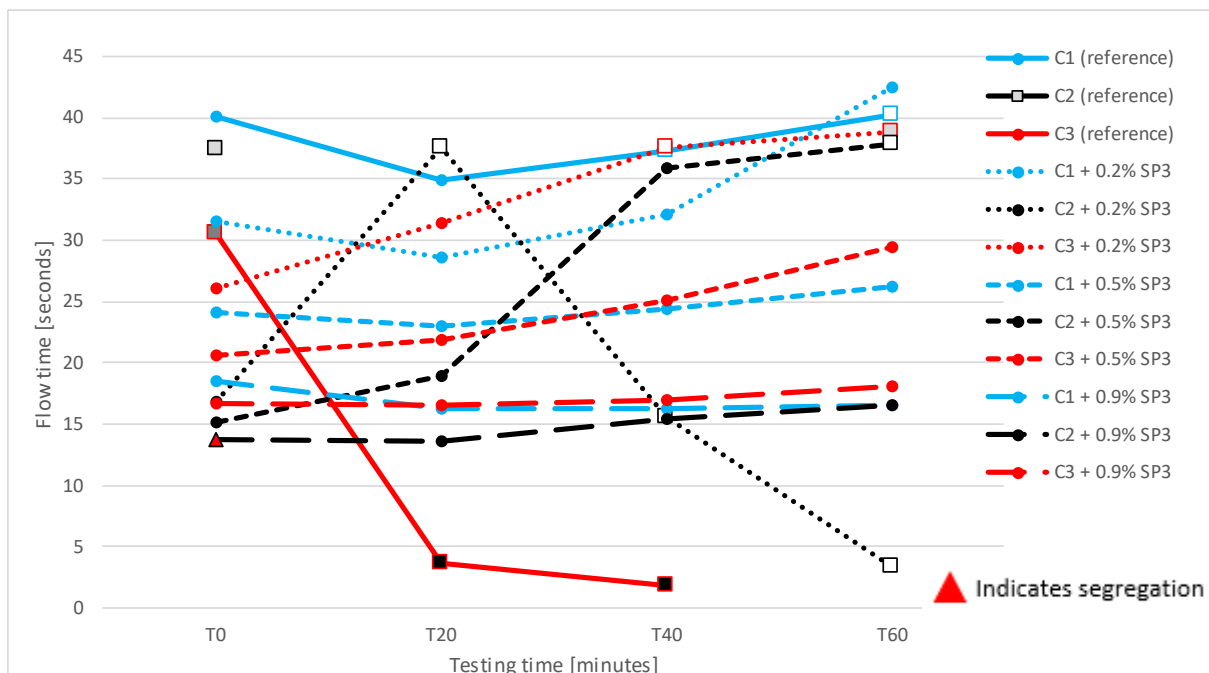


Figure 4.20: Marsh cone results for different clinkers in combination with SP3

SP4, the only naphthalene-based admixture proved to deliver interesting results as shown in Figure 4.21. For C1, the dosages of 0.2%, 0.5% and 0.9% superplasticiser respectively, decreased the flowability of the mix severely to such an extent that no test conducted resulted in the Marsh cone running empty, unlike the reference mix where the first two testing times delivered a clean result. The 0.5% dosage showed to be the least effective as the flow nearly immediately stopped at this dosage.

For C2, the dosages of 0.2% and 0.5% SP4 showed a positive effect on the workability at the 0 minute testing time, improving from the reference mix where the cone did not empty, to a result where a flow time could be measured without any paste remaining in the cone. The 0.5% dosage shows a bigger impact on the increase in flowability than the lower dosage of 0.2%. For both these dosages, only the 0-minute tests showed positive results with the tests conducted at the 20, 40 and 60 minute testing times showing the majority of the paste remaining in the cone. When considering the 0.9% dosage, the biggest increase in the flowability of the mix is shown at T0, with the flow time decreasing over time. However, at this dosage, the mix was able to flow through the Marsh cone without any of the paste remaining for all testing times considered, being the only mixture being able to give a clean result at all the times of testing using this superplasticiser.

C3 showed similar results as C1 when using SP4, seen in Figure 4.21. For all dosages of this superplasticiser, the paste could not empty the cone, leaving remaining paste in the Marsh cone for all the testing times. The 0.2% dosage resulted in a slight decrease in the amount of paste remaining in the cone while the 0.5% increased the remaining mixture by a small percentage. The 0.9% dosage increased the flowability of the mixture to such an extent that only 4% of the mixture remained in the Marsh cone after the 0 minute testing and around 17% after testing at time of 20 minutes, thereafter the remaining amount of paste increased over time to reach similar results to the other dosages.

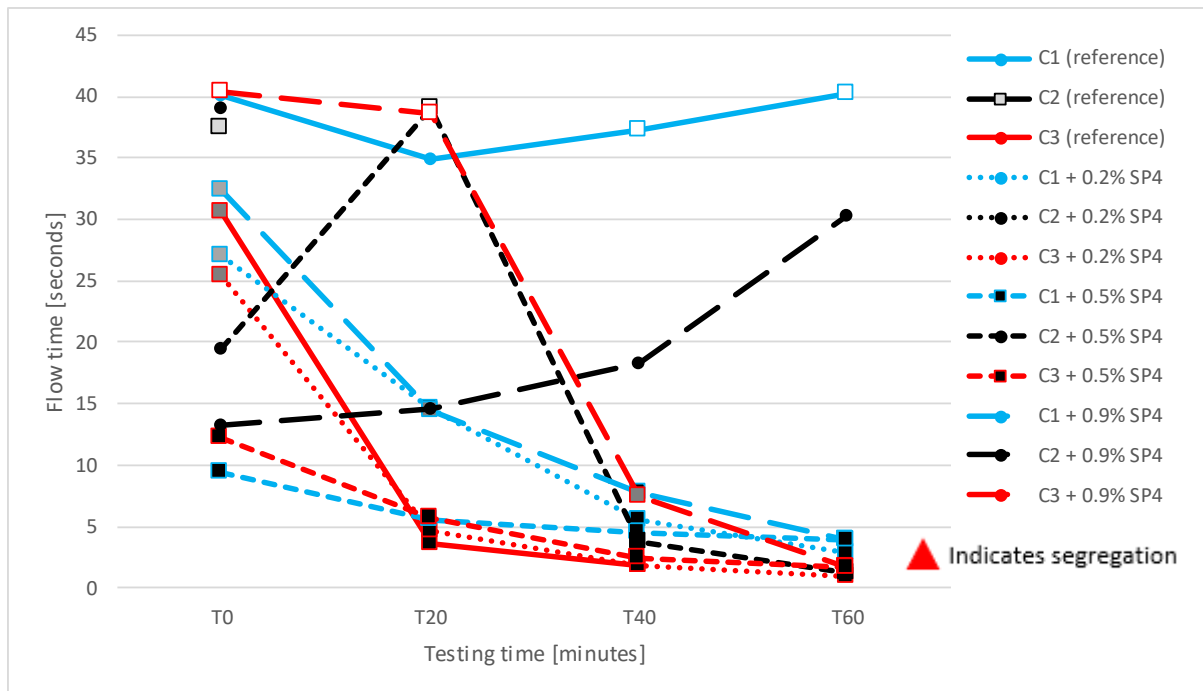


Figure 4.21: Marsh cone results for different clinkers in combination with SP4

These results, summarised in Section 4.2.3, confirm the study of Jayasree et al. (2008) who found that the Marsh cone flow time decreased as the dosage of superplasticiser is increased.

#### 4.2.4. Setting time

The effect of the addition of SP1 on the setting time of the various mixes can be seen in Figure 4.22. C1 resulted in a decrease in both the initial and final setting times for all three dosages considered, with the lowest dosage resulting in the biggest decrease in setting time, with the highest dosage resulting in the smallest decrease in setting times.

Figure 4.22 shows that for C2, the final setting times increased as the SP1 dosage increased, with a drastic increase being noted for the 0.9% dosage. A similar initial set was found for the 0.5% dosage to that of the reference mix, while the 0.2% dosage slightly decreased the initial setting time. For the 0.9% dosage, the initial setting time doubled for C2.

C3 was found to have similar initial setting times for both the 0.2% and the 0.5% dosages compared to that of the reference mix, while the final setting times were found to decrease slightly. For the 0.9% dosage, the initial setting time increased while a slight decrease in the final setting time was observed.

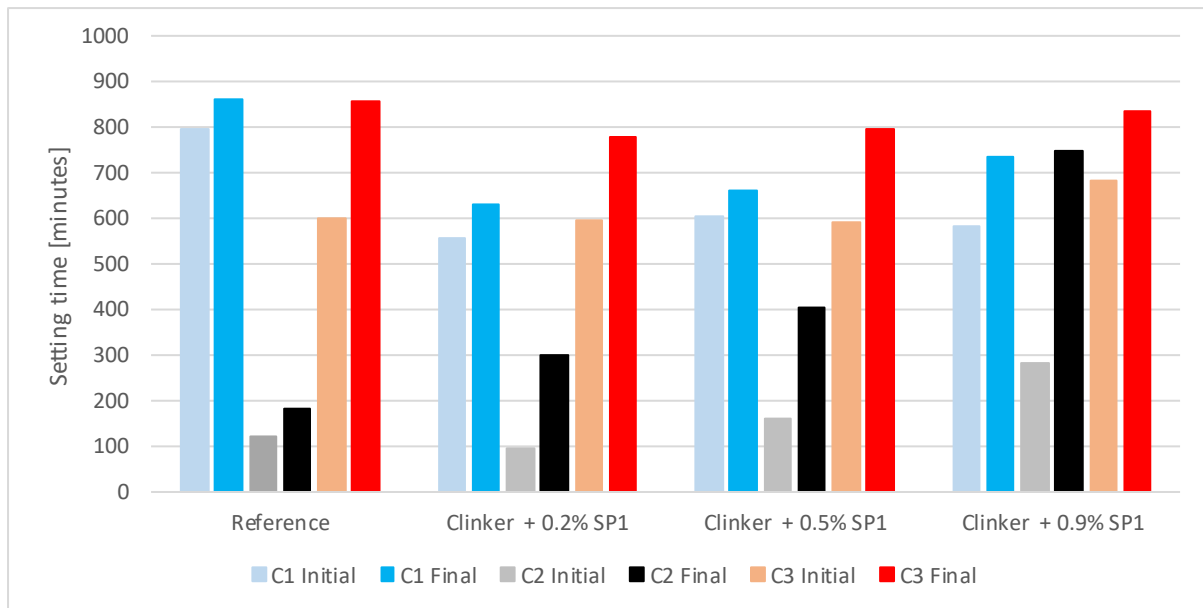


Figure 4.22: Setting time results for different clinkers in combination with SP1

The results of the SP2 additions can be seen in Figure 4.23. All three dosages considered resulted in a decreased initial and final setting time for C1, with the 0.2% dosage having a slightly lower setting time. C2 showed to have a similar initial setting time for both the 0.2% and 0.5% dosages to that of the reference mix, while the 0.9% addition resulted in a slight increase in the initial set. The final setting times for C2 was found to increase similarly for the 0.2% and 0.9% dosages, while that of the 0.5% dosage was found to be slightly higher. C3 showed a similar initial and final setting times for the 0.5% dosage SP2, while the 0.2% dosage was found to decrease both the setting times and the 0.9% dosage to increase the initial and final setting times, compared to that of the reference.

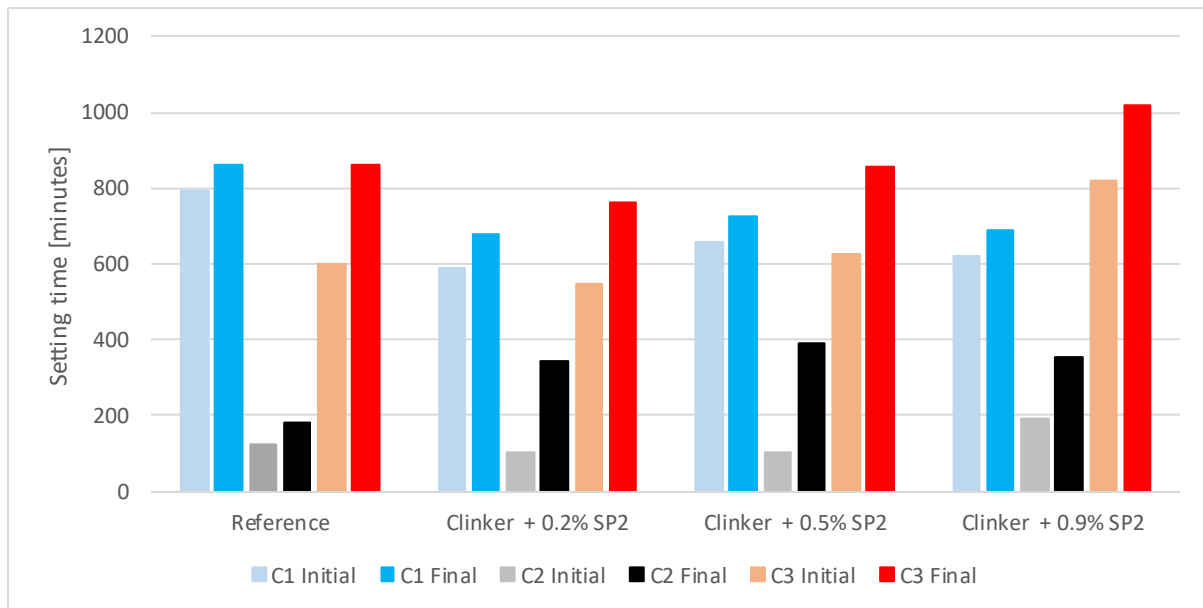


Figure 4.23: Setting time results for different clinkers in combination with SP2

Figure 4.24 contains the results when considering the effect of SP3. C1 showed a decrease in the initial set for all three dosages, resulting in a similar value for the dosages considered. The final setting times of the 0.2% and the 0.9% dosages was found to be roughly similar, both decreasing compared to the reference mix, while that of the 0.5% dosage increased in the final setting time. Similar initial setting times were observed for all dosages considering C2, indicating the SP3 does not have any significant impact on the initial setting time thereof. The final setting times of C2 with the 0.2% and 0.9% dosages showed the same slight increase compared to that of the reference mix, while a higher increase in final setting time was found for the 0.5% dosage. A similar, rather slight, decrease in final setting times for the 0.2% and 0.5% dosages was observed considering C3, while that of the 0.9% dosage increased quite significantly. The initial setting time of the 0.2% dosage declined slightly, while that of the 0.5% dosage showed a small increase compared to that of the reference mix. The 0.9% dosage was found to increase the initial setting time of C3 by more than 200 minutes.



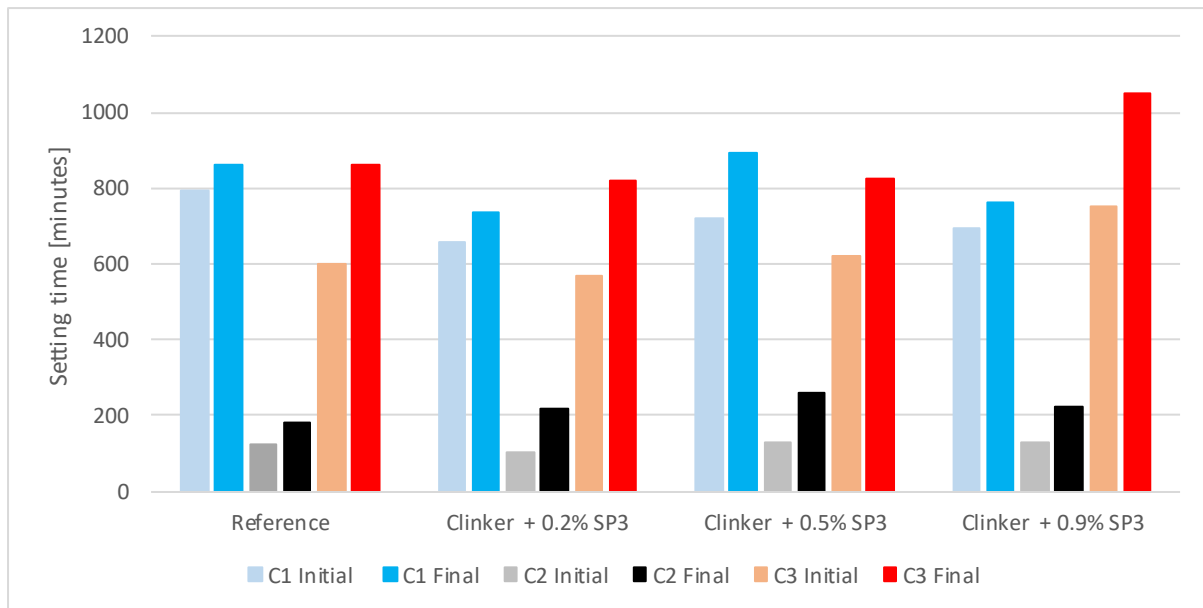


Figure 4.24: Setting time results for different clinkers in combination with SP3

Figure 4.25 shows the effect of SP4 on the setting times of a mix. Both the 0.2% and the 0.5% dosages were found to decrease the initial and final setting times of C1, while an increase was observed for the dosage of 0.9%. Little effect was observed on the initial setting time of C2 for all dosages considered, with the results being similar to that of the reference mix. For all the dosages, the final setting times of the mixes containing C2 was found to increase slightly, with the 0.5% dosage having a somewhat lower final setting time.

For C3, an increase in the initial setting time was observed for all the dosages considered, with that of the 0.2% and 0.5% being small compared to that of the 0.9% dosage, which increased drastically compared to that of the reference mix. Slightly higher final setting times were found for the 0.2% and 0.5% dosages when considering C3, while the 0.9% dosage resulted in the biggest increase in final setting time, reaching 1108 minutes compared to the reference final set time of 860 minutes.

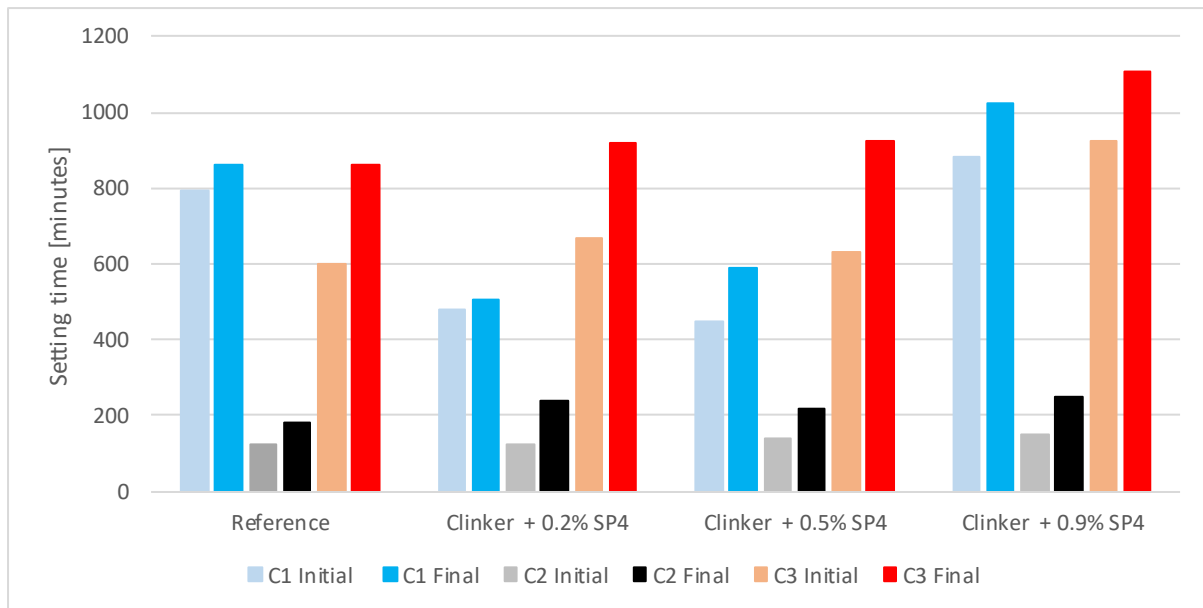


Figure 4.25: Setting time results for different clinkers in combination with SP4

#### 4.2.5. Compression strength

For C1, similar decreases in both the 2-day and 7-day compression strengths are shown in Figure 4.26 when adding 0.2% and 0.5% SP1 respectively, while for the 0.9% dosage, a slight decrease in the 2-day strength is noted with no change in the measured 7-day strength. Considering the influence on C2; the 0.2% dosage SP1 slightly decreased the strength of both the 2-day as well as the 7-day compression strength of the mix while the 0.5% dosage did not affect the strength of the reference mix at all. The 0.9% SP1 dosage is found to increase both the 2- and 7-day compression strengths of the mix. For C3, similar results compared to that of the reference mix is shown for both the 2- and 7-day compression strength tests, when considering the 0.9% superplasticiser dosage. These strengths decreased as the dosage superplasticiser decreased.

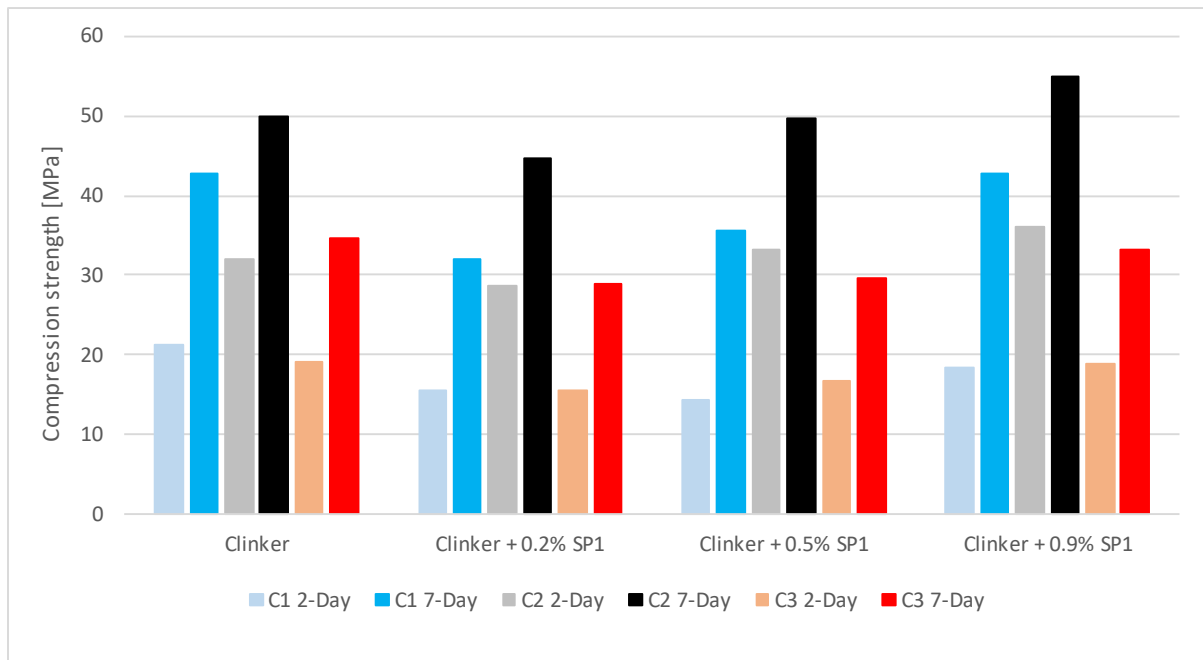


Figure 4.26: Strength test results for different clinkers in combination with SP1

The results for the strength tests for the mixes incorporating SP2 is shown in Figure 4.27. SP2 resulted in a decrease in compressive strength, with the highest being for the 0.5% dosage, followed by the 0.9% dosage and then, with the lowest loss in compressive strength, the 0.2% dosage. The loss in strength between the different dosages is much smaller for the 2-day results with only 1-2MPa difference compared to the 7-day results where the difference between dosages reached around 5MPa. The SP2 additions showed similar results to that of SP1 however, the decrease in strength for the 0.2% dosage is slightly more than that of the SP1 dosage, with the 0.5% dosage SP2 slightly lowering the compression strength compared to that of the reference mix. The 0.9% dosage also increased the strengths of the mix to find a 7-day compressive strength equal to that of the 0.9% SP1 dosage, with the 2-day strength being slightly lower compared to that of the SP1 addition. 0.2% dosage of SP2 resulted in similar strengths as the 0.2% dosage of SP1. These values slightly decrease for the 0.5% dosage, while a small increase in the 2-day strength is shown for the 0.9% dosage compared to that of the 0.5% dosage, not yet reaching the strength of the reference mix. The 7-day strength for the 0.9% dosage, on the other hand, resulted in a significant decrease, found to be similar to that of the 2-day compression strength.

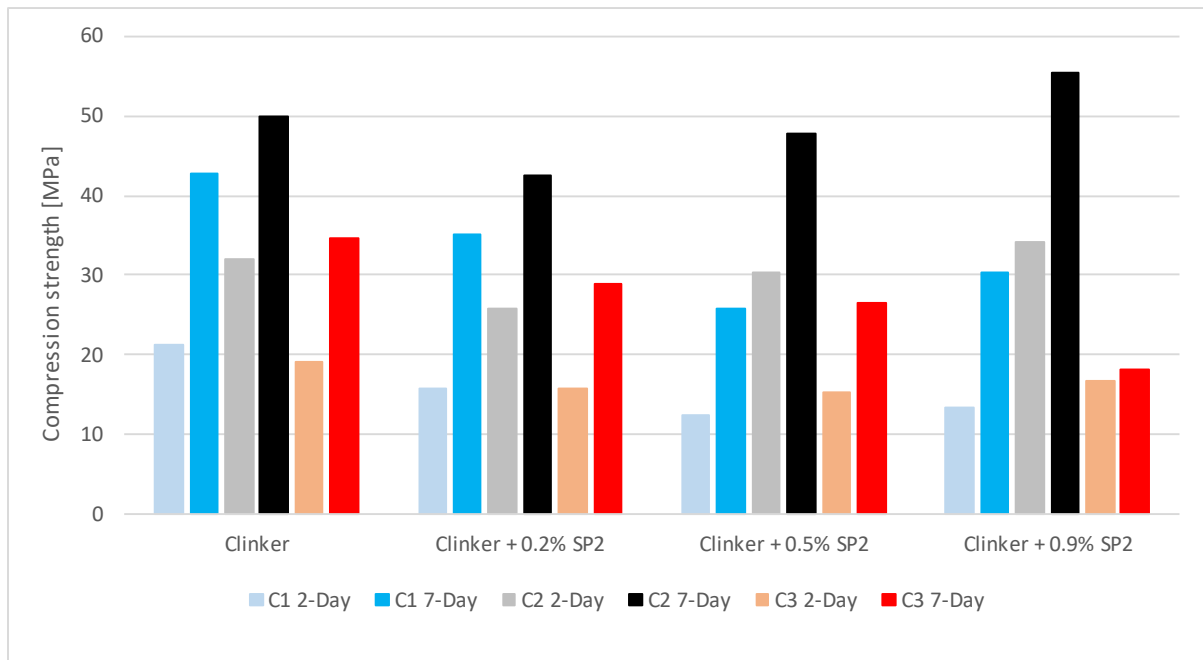


Figure 4.27: Strength test results for different clinkers in combination with SP2

Considering the various dosages of SP3 as seen in Figure 4.28, similar results were obtained for both the 2-day and 7-day strength tests. Again, the results obtained for the various dosages of SP3 was found to be similar to that of SP1. The 0.2% dosage resulted in a slight decrease in measured compression strengths for both the 2- and 7-day tests compared to that of the reference mix, while similar results are obtained for the 0.5% dosage than that of the reference mix, and for the 0.9% dosage, an increase in both the strengths is shown. SP3 shows a similar 2-day compression strength results for all the various dosages consider, being lower than that of the reference mix. The 7-day compression strength of the 0.9% dosage is close to that of the reference mix, while the 0.5% and 0.2% dosages are the same as the 7-day compression strength, with a value of 4MPa smaller than the 7-day strength of the 0.9% dosage.

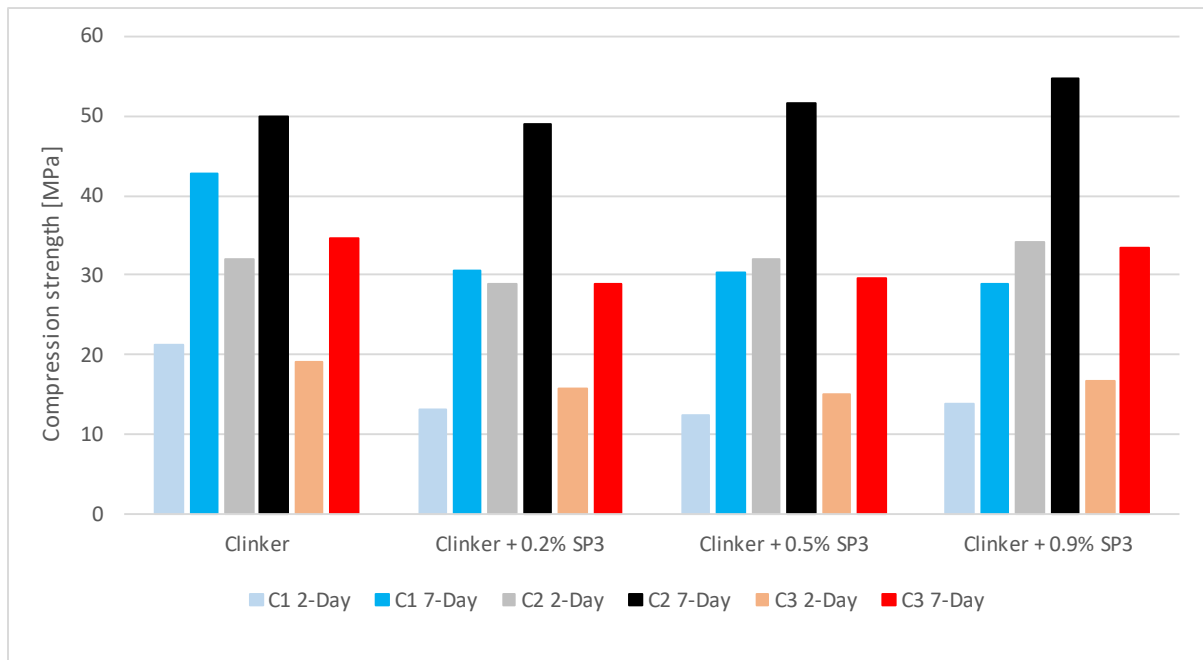


Figure 4.28: Strength test results for different clinkers in combination with SP3

While for SP4, with the results shown in Figure 4.29, the compressive strength for both the 2-day as well as the 7-day test declined as the superplasticiser dosage increased. Unlike with SP2, the biggest differences in the compressive strength is at the 2-day tests, around 3-4MPa while the difference in results for the 7-day tests is only around 2MPa. The addition of SP4 showed similar results for all three different dosages when considering the 2-day strength tests. These results are all nearly the same as the reference mix, suggesting the addition of SP4 does not affect the short-term strength gain of the paste. While similar results are also found for the 7-day tests for all the three different dosages, it can be observed to be slightly higher than that of the reference mix. For SP4, the 0.2% dosage resulted in 2- and 7-day strengths similar to that of the reference mix, with the compression strengths decreasing as the dosage superplasticiser increases. However, even with the largest dosage considered of 0.9%, the strengths do not deviate more than 3MPa from that of the reference mix.

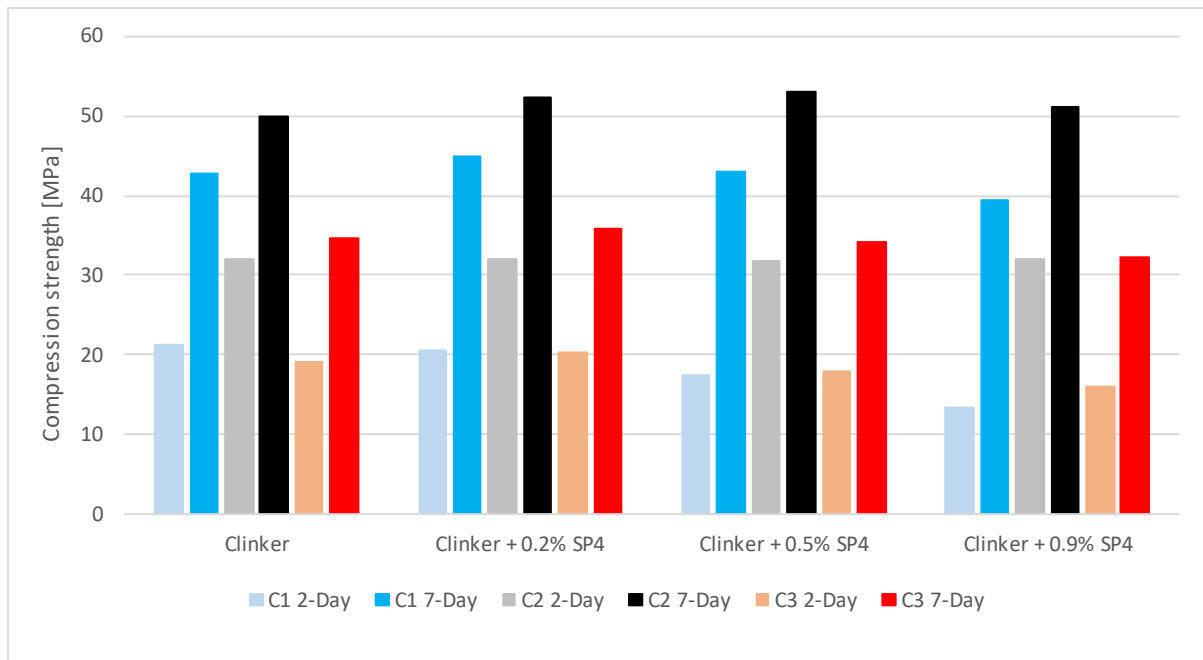


Figure 4.29: Strength test results for different clinkers in combination with SP4

#### 4.2.6. Concluding summary

Similar trends were observed for all four of the superplasticisers considered, with an initial increase in the flowability of the mixture which then decreases over time. The increase in flowability was related to the superplasticiser dosage, with a higher dosage resulting in a larger increase in flowability. For all superplasticisers considered, it was found that C2, which has a high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content while also having the highest total alkali content compared to the other clinkers, showed a more drastic decline in flowability after the initial testing time. SP4 was found to be the least effective when compared to the other superplasticisers as it showed the smallest increase in flowability.

Considering the Marsh cone tests, it is shown that for SP1 used at higher dosages, 0.5% and 0.9% respectively, the mixture containing C2 segregated at the 0 minute testing time, while for SP2, both C2 and C3 segregated at the 0 minute testing time. SP3 showed again segregation at the high dosage measured at 0 minutes, but only for C2. These three PCE superplasticisers were found to be more effective at higher dosages, as well as being able to better maintain a constant flowability at these higher dosages. SP4 was found to be least effective. For all mixes containing both C1 and C3, there was paste remaining in the Marsh cone after testing for all the dosages considered, while C2 was shown to increase flowability when used with SP4, the flowability decreased again shortly with time.

A slight increase in setting times is shown for the additions of superplasticiser, with the setting times increasing as the dosage of superplasticiser increases. SP1 has the biggest effect on the setting time

of C2, especially at the 0.9% dosage, while SP3 has the most significant effect on the setting time of C1, and SP4 on that of C3. It is further observed that slight variations in the compression strengths of the mixes occur with the addition of superplasticiser, however, there was not a single increase or decrease in strength that stood out compared with the other results.

### 4.3. Sulphate content and type

In this section, the effect of bassanite and gypsum, as binder substitution, is discussed to determine the interaction thereof when used in combination with the different chemical compositions of the clinker.

#### 4.3.1. Sulphates compositions

The following chemical compositions shown in Table 4.3, in percentage, was found using both the XRF analysis and the wet SO<sub>3</sub> analysis (SANS 50196-2:2014), for the bassanite and gypsum respectively.

Table 4.3: Chemical composition of bassanite and gypsum

<b>Sample Reference</b>	<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>Mn<sub>2</sub>O<sub>3</sub></b>	<b>TiO<sub>2</sub></b>	<b>CaO</b>	<b>MgO</b>
Bassanite	0.53	0.07	0.00	0.00	0.00	39.5	0.76
Gypsum	0.65	0.09	0.04	0.00	0.02	36.9	0.60
<b>Sample Reference</b>	<b>P<sub>2</sub>O<sub>5</sub></b>	<b>Wet SO<sub>3</sub></b>	<b>Cl</b>	<b>K<sub>2</sub>O</b>	<b>Na<sub>2</sub>O</b>	<b>LOI</b>	<b>Total</b>
Bassanite	0.019	52.54	0.001	0	0.006	5.98	99.363
Gypsum	0	49.88	0.003	0.016	0	10.9	99.134

Both samples have a CaSO<sub>4</sub> content greater than 85%. The chemical formula of bassanite was determined to be CaSO<sub>4</sub>·0.5H<sub>2</sub>O while the gypsum was determined to have the chemical formula of CaSO<sub>4</sub>·2H<sub>2</sub>O. From the EDS analysis, it was found that the gypsum has a higher calcium content than the bassanite.

#### 4.3.2. Mini slump

For C1, a similar decrease in initial slump flow occurred for the 2% and 4% bassanite additions as shown in Figure 4.30. A steady decline in slump flow is observed for the 4% addition between testing times 0 and 40 minutes, where no slump flow occurred, while the 2% addition caused a drastic decrease in slump flow to reach the zero-slump flow at 20 minutes. The 6% bassanite addition resulted in a bigger loss in initial slump flow, but a reduced gradient is noted in the decrease of slump flow for this addition over time. Adding 2% and 6% gypsum respectively resulted in a similar initial slump flow value, seen in Figure 4.31, found to be much lower than the bassanite additions. The 2% gypsum



addition caused a rapid loss in slump flow, measured to be zero at 20 minutes, while the 6% gypsum addition gradually decreased the slump flow of the mixture over time.

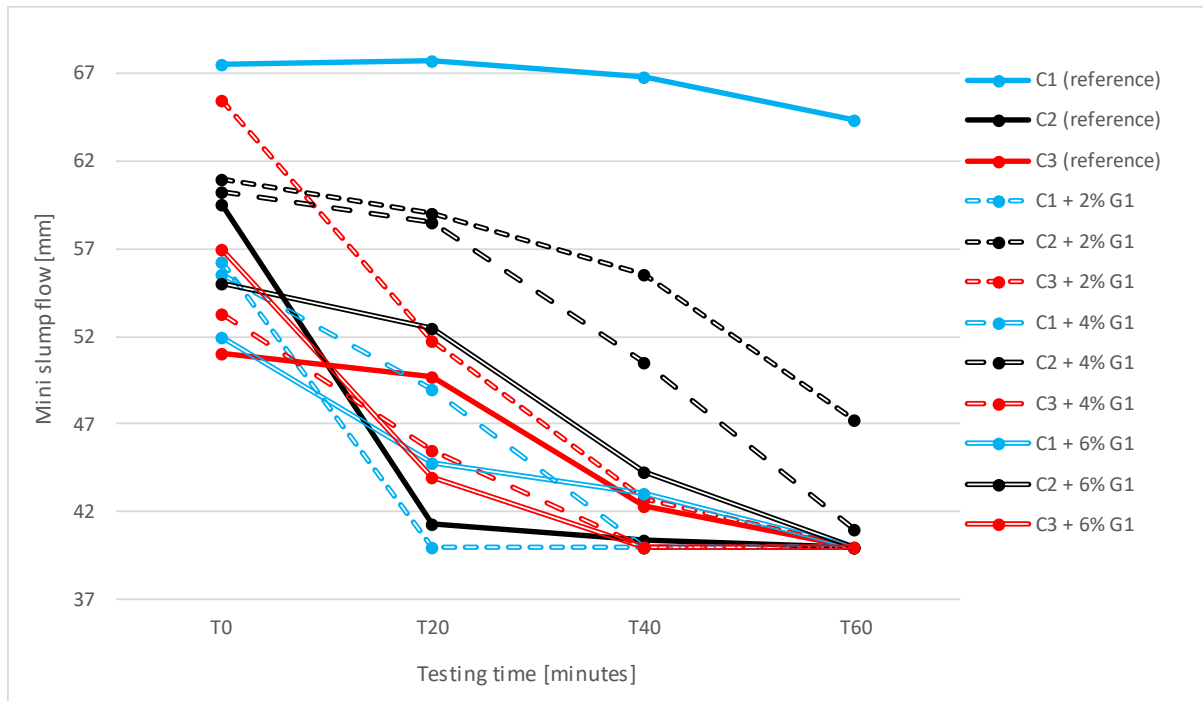


Figure 4.30: Mini slump test results for different clinkers with the addition of bassanite

Considering C2 in Figure 4.30, the 6% bassanite addition is the only addition considered to lower the initial slump flow of the mix compared to that of the reference mix. Adding 2% - and 4% bassanite is shown to result in a similar initial slump flow than that of the reference mix, but unlike the reference, the slump flow of these two additions decreased more steadily over time. Adding 6% bassanite decreased the slump flow over time. For C2 as found in Figure 4.31, the 2% and 6% gypsum additions resulted in similar initial slump flows, measured to have the biggest increase in slump flow, the decrease in slump flows of these two additions followed a similar trend to eventually, result in a similar slump flow measured at the end of the testing period.

For C3, all of the additions considered improved the initial slump flow measured compared to that of the reference mix. The 4% and 6% bassanite, as well as the 2% and 6% gypsum additions, affected the slump flow of the mix similarly, increasing the initial slump flow and the decrease in slump over time following a similar pattern, as seen in Figures 4.30 and 4.31 respectively. The 2% bassanite resulted in the biggest increase in initial slump, also having higher values measured at testing times of 20 and 40

minutes, but also reaching a slump flow value of zero at the end of the testing period, as do all the other mixes considered using C3.

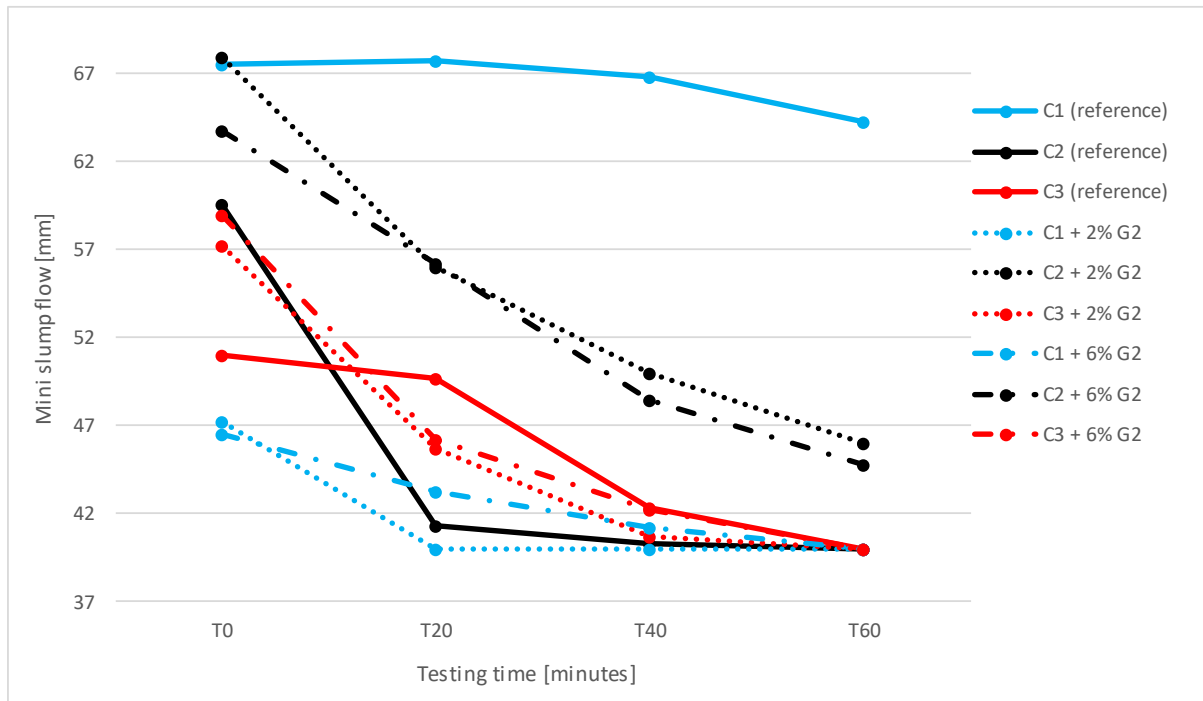


Figure 4.31: Mini slump test results for different clinkers with the addition of gypsum

The surface area analysis results, found in Table 3.2, indicates basanite having the biggest surface area compared to that of the various clinkers as well as the gypsum. The particle size distribution in Figure 3.6 showing that C2, while having a smaller surface area, has a similar size distribution than that of the bassanite. From Figure 4.30, no distinctive trend can be found for the various additions of bassanite. This lack of a pattern when considering the low-, medium- and high additions of bassanite suggest that the increased surface area of the bassanite compared to that of the clinkers does not have such a pronounced effect on the flowability of the mix, like that of the chemical reaction between the clinkers and the bassanite.

From the results obtained in Figure 4.31, a similar trend in both the lower addition of 2% as well as the higher 6% gypsum addition, was found. This result suggests that the difference in particle shape and size of the gypsum, compared to that of the clinkers, did not have a significant effect on the flowability of the mix, with the chemical aspect of the additions governing the change in flowability. The particle size distribution, depicted in Figure 3.6, showed C2 having a very similar distribution to

that of the gypsum. The increased flowability of C2 with the addition of gypsum compared to the reference, confirms this conclusion.

#### 4.3.3. Marsh Cone

For C1, the 2% gypsum results in a much lower flowability than the 2% bassanite addition as shown in Figure 4.33 however, for both of these two additions the mixture false set just after the initial testing period. From Figure 4.32, the addition of 4% bassanite was found to have a similar effect on the flowability of the mixture as the 2% bassanite, however, no false set occurred at this addition. With both the 6% bassanite and 6% gypsum additions, the flowability was found to drastically decrease. The 6% bassanite addition resulted in a longer initial flow time with less paste remaining in the cone than the 6% gypsum addition where the continuous flow stopped much quicker, leaving behind a larger percentage of the paste.

Considering C2 in Figure 4.32 and 4.33, the 2% bassanite and the 2% and 6% gypsum additions improved the flowability of the mix compared to that of the reference mix, as a larger percentage of the paste cleared the cone before the continuous flow stopped. The gypsum and bassanite additions showed barely any difference in results, suggesting the chemical composition of the gypsum played a small role in the reaction. The 4% bassanite showed a similar initial result to that of the reference mix, while larger quantities of paste remained in the cone after testing at the other testing times when compared to the reference mix where only a few drops were observed. The 6% bassanite addition was found to decrease the flowability of the mix, resulting in nearly double the amount of paste to remain in the Marsh cone than that of the reference mix.

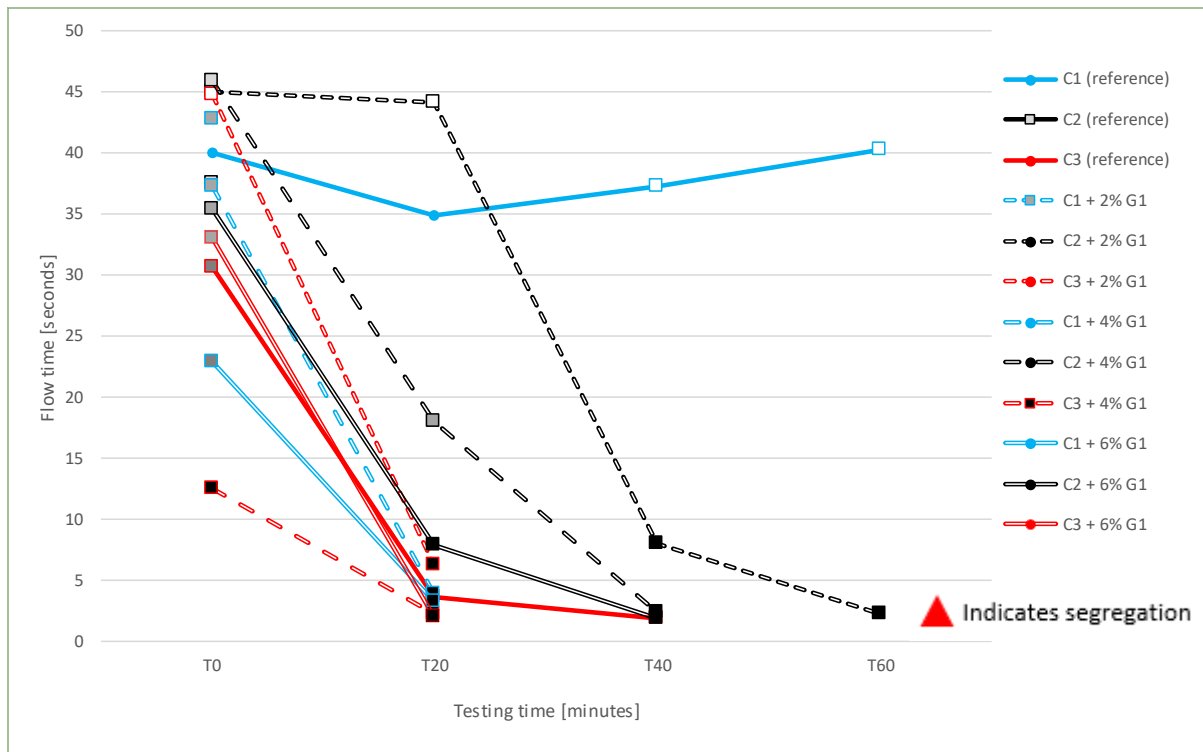


Figure 4.32: Marsh cone test results for different clinkers with the addition of bassanite

When considering C3 together with the various additions of bassanite and gypsum, similar results were found for all the additions considered at testing times 20, 40 and 60 minutes, where between 86% and 94% of the paste remained in the cone for time 20 minutes and the continuous flow only lasted a few seconds, and times 40 and 60 minutes resulting only in a few drops being observed.

Considering both Figure 4.32 and 4.33, the 2% bassanite addition showed similar initial results to that of the 6% gypsum addition, where a long continuous flow time was observed with a small percentage of paste remaining in the cone. Whereas the 6% bassanite addition showed similar initial results than the 2% gypsum addition, having longer continuous flow times, similar to that of the two additions discussed before, however with these additions, more paste was found to be left remaining in the flow cone. The 4% bassanite addition showed the unique results having a short time of continuous flow with about 80% of the mix remaining in the cone.

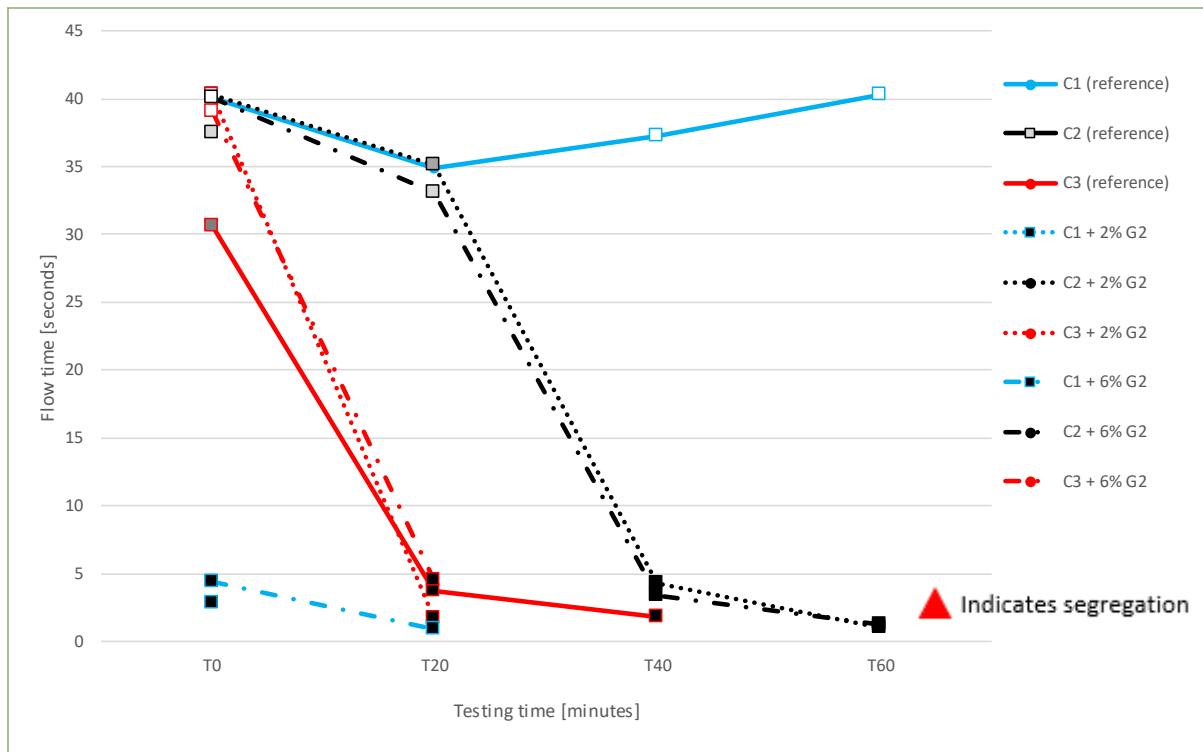


Figure 4.33: Marsh cone test results for different clinkers with the addition of gypsum

#### 4.3.4. Setting time

C1 with high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content shows high initial and final setting times as shown in Figure 4.34. As the addition of bassanite increased, these setting times decreased, showing a larger period of time between initial and final set for the 2% addition, with the period between initial and final set decreasing as the addition of bassanite increases to 4% and 6%. Similar initial set occurred for both the 2% addition of bassanite as well as the 2% addition of gypsum, while the final set occurred much later on for the bassanite addition than for the gypsum. Comparing the 6% bassanite and 6% gypsum additions, the initial and final set for the gypsum took longer than for the bassanite addition, while similar periods between initial and final set was observed.

C2, with a high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content, showed a much lower initial and final setting times compared to that of the other two clinkers, as shown in Figure 4.34. The addition of 2% bassanite and 2% gypsum respectively did not have much of an influence on the initial setting time of the mix, but the 2% gypsum showed to decrease the final setting time slightly, while a similar final set occurred for the 2% bassanite addition to that of the reference mix. Adding 4% bassanite reduced both the initial and final setting times of the mix, showing a similar result than the addition of 6% gypsum. The period between the initial and final set for these two mixes is similar to that of the reference and 2%

bassanite addition mixes. The 6% bassanite addition resulted in low initial and final setting times with there being only 23 minutes between these two values.

For the reference mix of C3 with high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  contents, as seen in Figure 4.34, the longest period between initial and final set was recorded, with this clinker having a final setting similar to that of C1, suggesting the chemical composition of C3 favours initial set, but then takes a longer time to reach final set.

Adding bassanite and gypsum reduced these setting times significantly. The 2% bassanite addition showed a similar effect on the setting times as the 6% gypsum addition, reducing both initial and final set. Adding 2% gypsum also reduced the initial setting time to a similar time than the additions mentioned previously, the period between initial and final set was shorter since the 2% gypsum addition resulted in a lower final setting time. For the 4% bassanite addition, the initial setting time was similar to the 2% bassanite addition with the final setting time being much lower than that of the 2% addition. Increasing the bassanite addition to 6% lowered both initial and final setting times of the mix, showing a much faster set when comparing to the 6% gypsum addition.

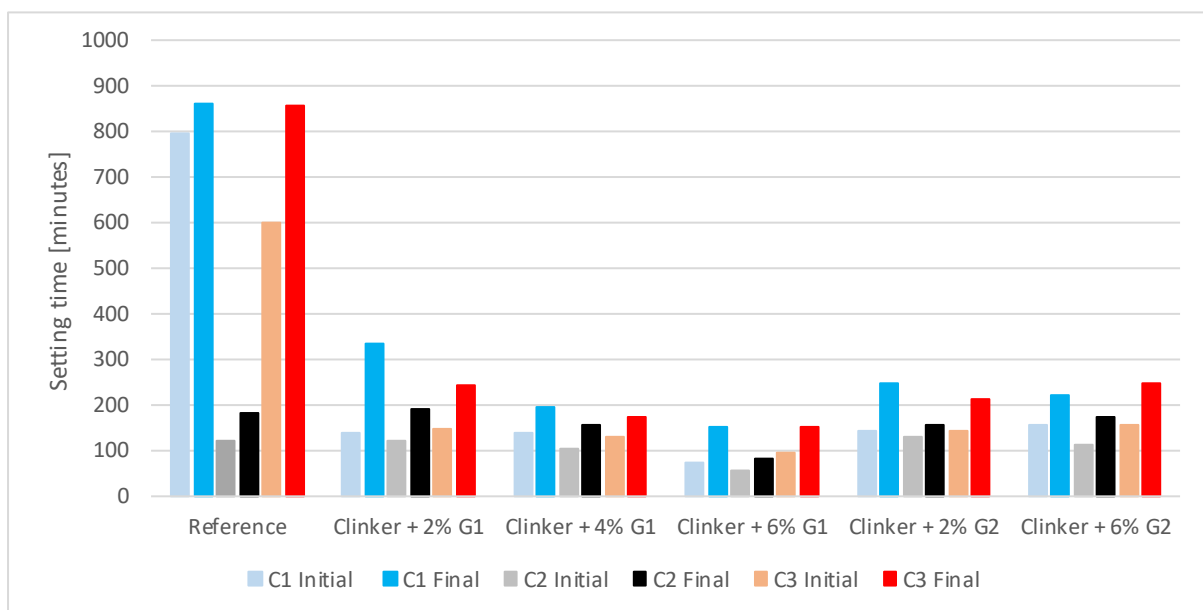


Figure 4.34: Setting time results for different clinkers with the addition of bassanite/gypsum

#### 4.3.5. Compression strength

In Figure 4.35, C1 showed a similar decrease in both the 2 and 7-day compressive strengths measured for the 2% bassanite and 2% gypsum additions. The 6% bassanite and 6% gypsum additions increased

the 2-day compressive strengths to reach a similar value, while the 7-day strengths at these additions are similar to that of the reference mix. This suggests that there is no real difference in the interaction on pure clinker between gypsum and bassanite, with the higher additions affecting the short-term strengths more severely than the long-term strengths. The 4% bassanite addition resulted in a 2-day compressive strength similar to that obtained by the 6% additions, while the 7-day strength was measured to be slightly higher than that of the 6% additions.

The addition of 2% bassanite caused the biggest decrease in the 7-day strength of the mix containing C2, seen in Figure 4.35, with the 4% bassanite and 2% gypsum resulting in a similar strength loss for the 7-day compressive strength and the 6% gypsum and 6% bassanite additions having the same slight increase in compressive strength measured at 7 days. The 2% bassanite decreased the 2-day strength more than that of the 2% gypsum addition. The 4% bassanite addition increased the 2-day compressive strength slightly with there being a 10 MPa difference between the 2% and 4% additions. A similar increase in the 2-day compressive strength occurred for the 6% bassanite and 6% gypsum additions, with the gypsum addition, have a strength of 3 MPa higher than that of the bassanite addition, suggesting a higher increase in bassanite is needed to achieve the same results than gypsum at low dosages when considering early strength gain.

For C3, a similar result is shown compared to the reference mix for all the additions considered, seen in Figure 4.35. With all of the additions increasing the 2-day compressive strength while the 2% bassanite and gypsum additions slightly lowering the strength and the 4% bassanite and 4% and 6% gypsum additions slightly increasing the strength of the 7-day tests. These increases and decreases in the strength of the mixes are so small that it can almost be ignored.



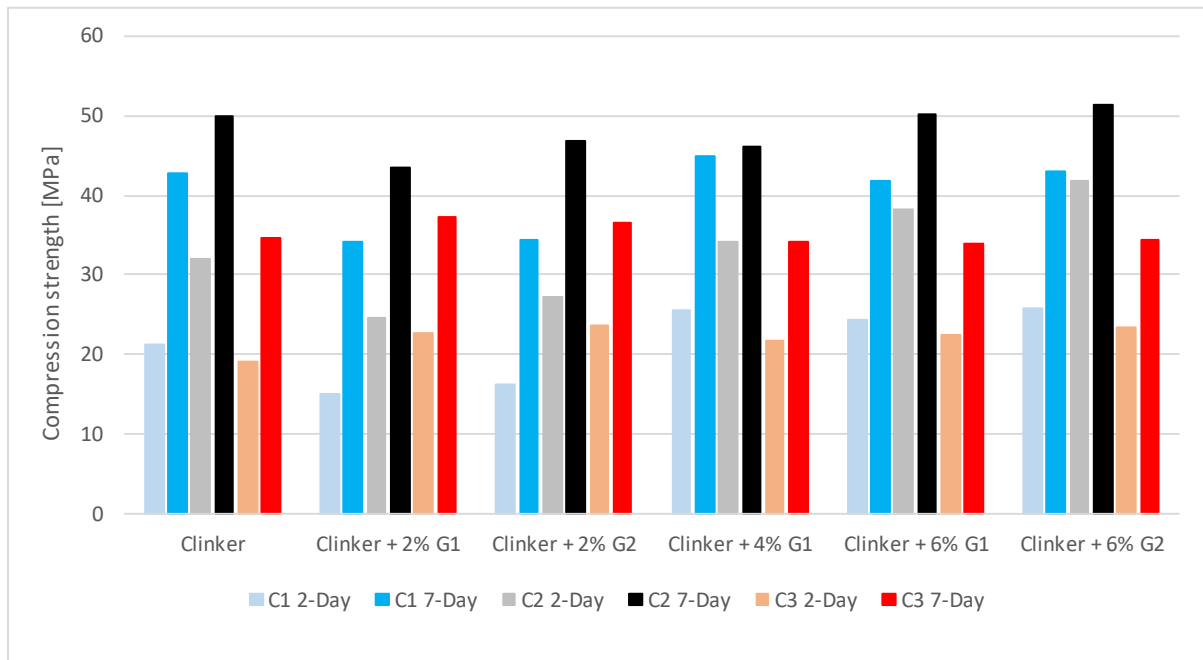


Figure 4.35: Strength test results for different clinkers with the addition of bassanite/gypsum

#### 4.3.6. Concluding summary

While the setting times decreased significantly for C1 and C3 with the bassanite/gypsum additions, the setting times of the C2 mixes remained fairly constant for the additions considered. Although the additions decreased the setting times of the various mixes, the strength thereof seems to be unaffected. The addition of gypsum and bassanite respectively, reduced the overall flowability of the mixes considered, while also increasing the paste remaining in the Marsh cone after testing. For the 2% bassanite and gypsum additions, false set was observed for C1 only, which has a high  $C_4AF$  content and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content with the lowest total alkali compared to the other clinkers.

When considering the Marsh cone- and mini slump test results, it was found that a similar change in flowability occurred for the low- and high gypsum additions, while for the low- and high additions of bassanite, the change in flowability varied quite significantly. This could suggest that the hemihydrate phase of calcium sulphate is more reactive in combination with clinker than that of the dihydrate.

## 5. COMBINED RESULTS OF CLINKER, SUPERPLASTICISER AND SULPHATES

This section investigates the effect an addition of bassanite has on the effectiveness of superplasticisers. 2% and 6% bassanite additions as a binder substitute are considered in combination with 0.2% and 0.9% superplasticiser dosages. These values are chosen to test high bassanite addition with low superplasticiser dosages; low bassanite with high superplasticiser, low bassanite as well as low superplasticiser and high bassanite additions in an attempt to identify compatibility issues.

### 5.1. Gypsum and superplasticisers combined

In this section, the addition of gypsum on the effectiveness of the superplasticisers is investigated. Only 6% additions of gypsum were considered for testing with superplasticiser. As the amount of clinker available for testing was limited and the results of the bassanite addition found to govern, only a small number of tests was considered with the gypsum addition. The 6% dosage was preferred to that of the 2% dosage, as the focus of this study falls on the reaction between the added sulphate and the superplasticiser, which motivated the higher gypsum addition.

These mixes were also only considered for the 0.9% superplasticiser dosages. Again, it was taken into account that only a limited number of tests were able to be conducted with regards to the gypsum addition. It was decided to determine the effect of a high gypsum addition on that of a larger dosage superplasticiser, arguing that these higher additions would be more likely to cause a compatibility issue than lower additions, as there is a larger amount of materials to interact with each other.

#### 5.1.1. Mini slump

With the addition of 6% gypsum, similar results were obtained for C1 and C2, when considering the effect of SP1 as shown in Figure 5.1. Both these mixes showed a similar initial slump flow, with a value slightly lower than that of C2, while both these mixes followed a similar trend in the slump loss over time. A slight increase in slump flow was observed for C2, whereafter at testing time of 40 minutes, the mix started to decrease in flowability. This suggests the effectiveness of the superplasticiser increases for up to 40 minutes for C2 before it decreases in flowability again, while for C1 and C3, the effectiveness of the superplasticiser decreased straight away, albeit only slightly during the first 20 minutes

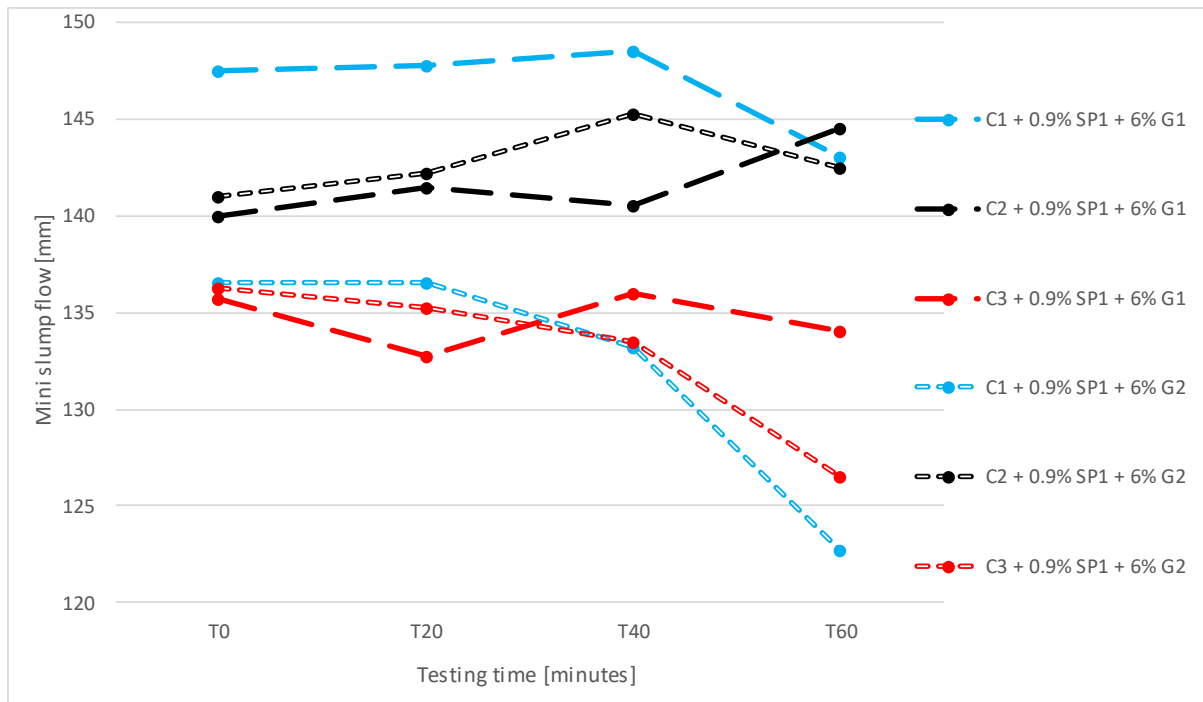


Figure 5.1: Mini slump test result for different clinkers in combination with 0.9% SP1 and bassanite/gypsum

Unlike for SP1 where C1 and C3 showed similar initial slump flow values with the addition of 6% gypsum, SP2 shows that C1 and C2 show similar initial slump flow values, with that of C3 being slightly lower as shown in Figure 5.2. C1 immediately showed a loss in flowability after the initial testing time, indicating that the superplasticiser was decreasing in effectiveness from the start.

C2 and C3 resulted in a steady increase in slump flow over time, as the superplasticiser improved in effectiveness. This continued over the entire testing period for C2, while at testing time of 40 minutes, C3 started to show a decrease in slump flow, suggesting the superplasticiser decreasing in effectiveness.

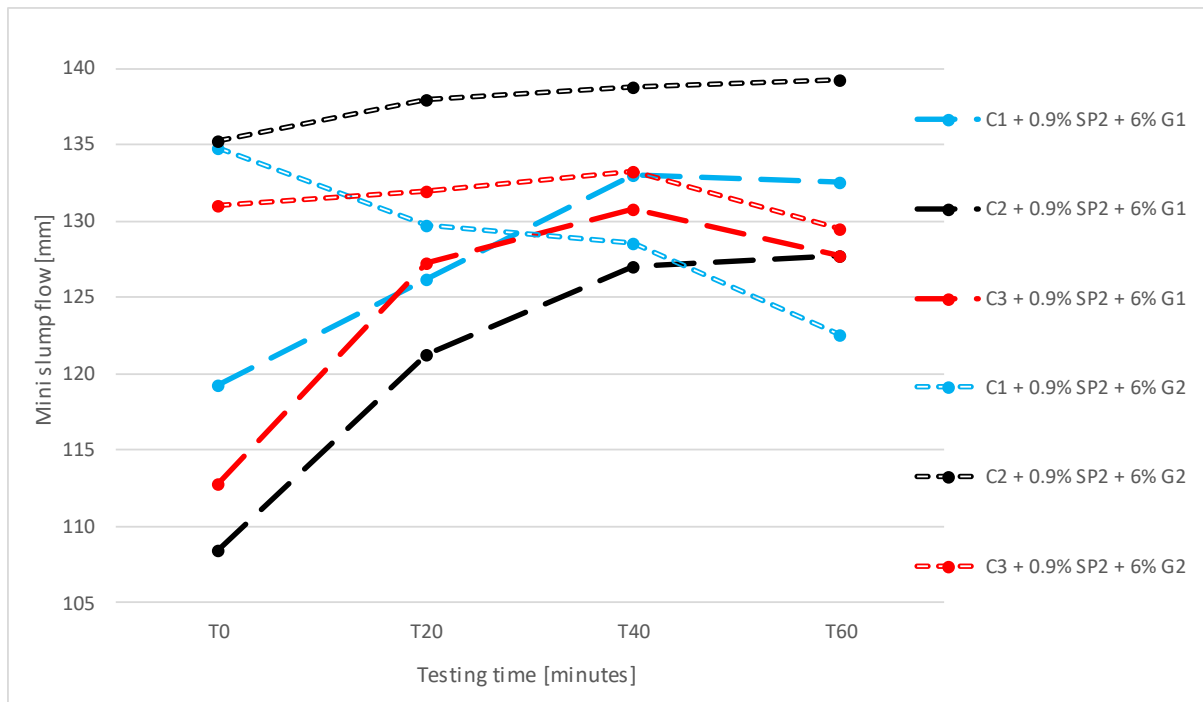


Figure 5.2: Mini slump test result for different clinkers in combination with 0.9% SP2 and bassanite/gypsum

For SP3, similar results to that of SP2 is shown for C3 in Figure 5.3, where an increase in flowability is observed, with a decrease in the slump flow is observed after testing time of 40 minutes, when the superplasticiser is believed to decrease in effectiveness. C1 also showed similar results for SP3 compared to that of SP2. Again, the highest measured slump value was measured initially, with a gradual decrease in this flowability observed over time. Contrary to the results obtained for C2 when using SP2, where an increase in flowability was observed over the entire testing period when using SP3, the highest measured slump flow was measured at the testing time of 0 minutes, with the flowability of the C1 and C2 mixes decreasing over time.

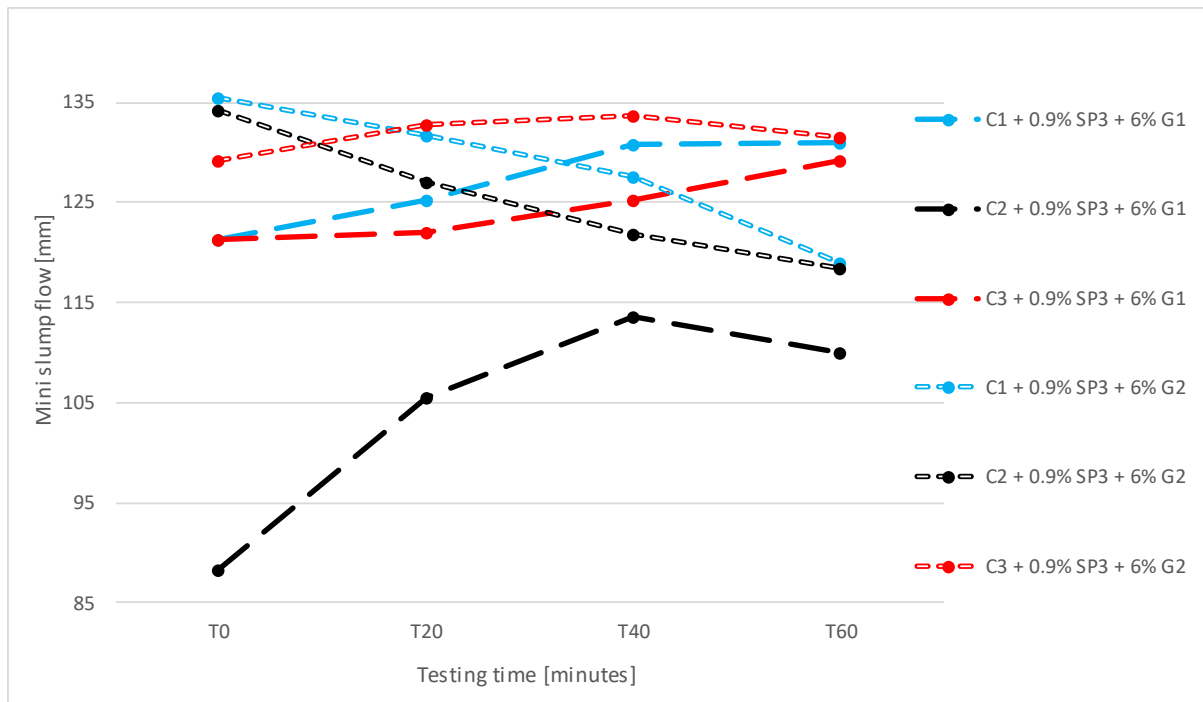


Figure 5.3: Mini slump test result for different clinkers in combination with 0.9% SP3 and bassanite/gypsum

SP4 resulted in a decrease in slump flow over time for all mixes considered as shown in Figure 5.4. C2 and C3 showed a similar gradient in the loss of flowability over time, while that of C1 occurred more rapidly. SP4 is also much less effective in increasing the flowability of a mix compared to that of the PCE superplasticisers considered.

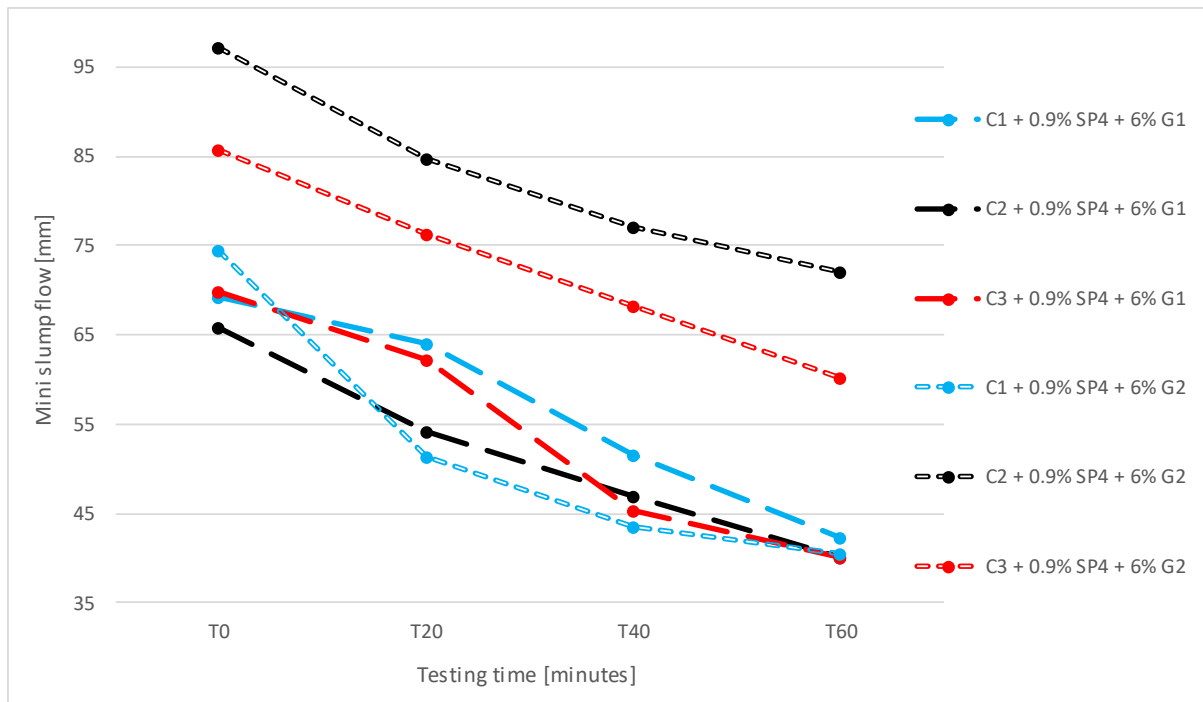


Figure 5.4: Mini slump test result for different clinkers in combination with 0.9% SP4 and bassanite/gypsum

### 5.1.2. Marsh Cone

With the dosage of 0.9% SP1 in combination with 6% gypsum, it is shown in Figure 5.5 that the mixes containing C2 and C3, segregated at each of the testing times considered, while for C1, segregation was only observed at testing times of 0 and 20 minutes. The flow time of C3 is fairly constant over the testing period, while that of C2 and C3 decreased over time, which describes an increased flowability. C1 however, after the testing time of 40 minutes, again showed an increase in the flow time, suggesting the mixture decreases in flowability as the effectiveness of the superplasticiser decreases.

For SP1, segregation was found to occur at all testing times considered, for all three clinkers when considering both the addition of 6% bassanite and 6% gypsum, with the exception of C1 in combination with 6% gypsum.

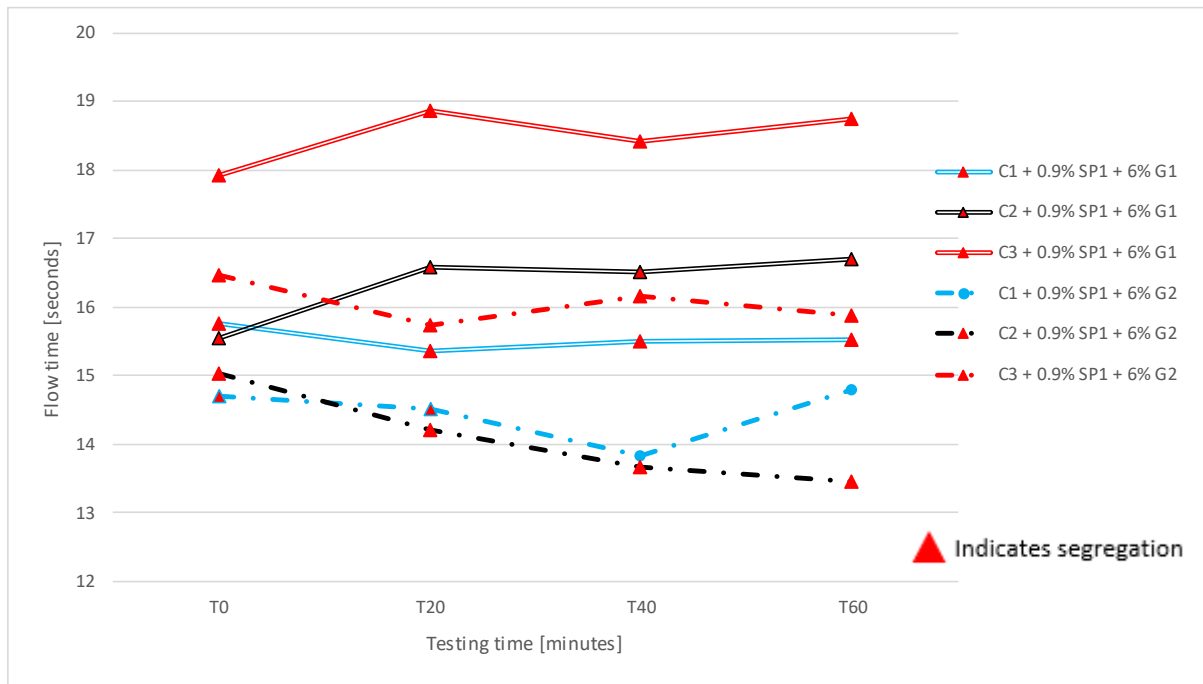


Figure 5.5: Marsh cone test result for different clinkers in combination with 0.9% SP1 and bassanite/gypsum

Considering SP2, C2 shows the shortest flow time and highest workability, with a slight increase in workability, observed gradually over the testing period as shown in Figure 5.6, for the 6% gypsum addition, while 6% bassanite decreased the workability of the mix significantly at time = 0 minutes. C1 showed to have a slightly lower increase in workability than that of C2 initially, while maintaining a constant flow time over the testing period considered, with a small increase in flow time observed after testing time of 40 minutes. C3 has the lowest flowability of the three clinkers considered, with segregation taking place at all testing times. Although a decrease in the flow time is noted for C3 over time, it eventually increases again after 40 minutes of mixing.

For SP2, only C3 segregated with the addition of 6% gypsum, while all other combinations considered showed no cumbersome deviations.

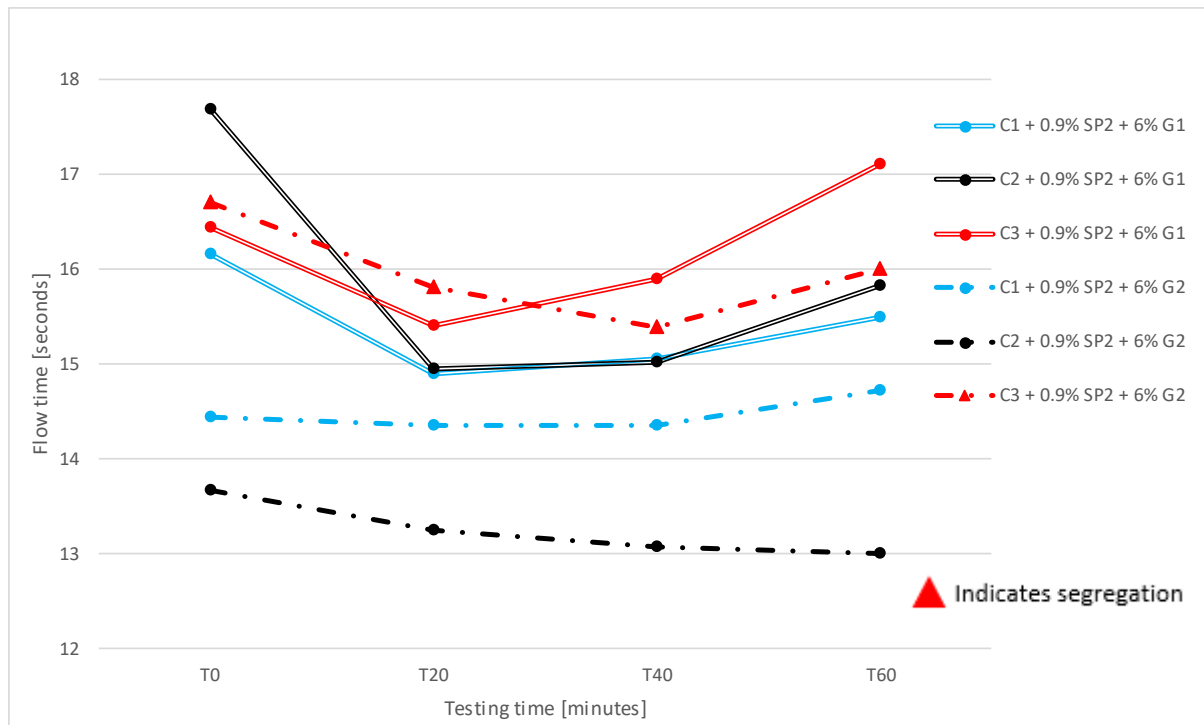


Figure 5.6: Marsh cone test result for different clinkers in combination with 0.9% SP2 and bassanite/gypsum

Considering Figure 5.7 and the 6% gypsum addition, C1 and C2 showed similar initial and final flow times for the SP3 addition, however, for C1 the flow time increases over time and the decreasing again, while first, a decrease in flow time, followed by an increase occurred for C2. These differences in the flow time curves suggest the effectiveness of the superplasticiser peaks at different times for the different clinkers. Again, as with SP2, C3 was the only clinker that segregated for the first three testing times where after a normal, cohesive flow was observed. C3 showed the smallest initial flowability, which however improved over the testing period to result in a final flow time slightly lower than that of the other two clinkers.

Compared to the gypsum addition, the 6% bassanite addition resulted in a similar improvement in workability for C1. Both C2 and C3 showed a lower workability when adding 6% bassanite, with the biggest decrease being found for C2 at testing time = 0 minutes.



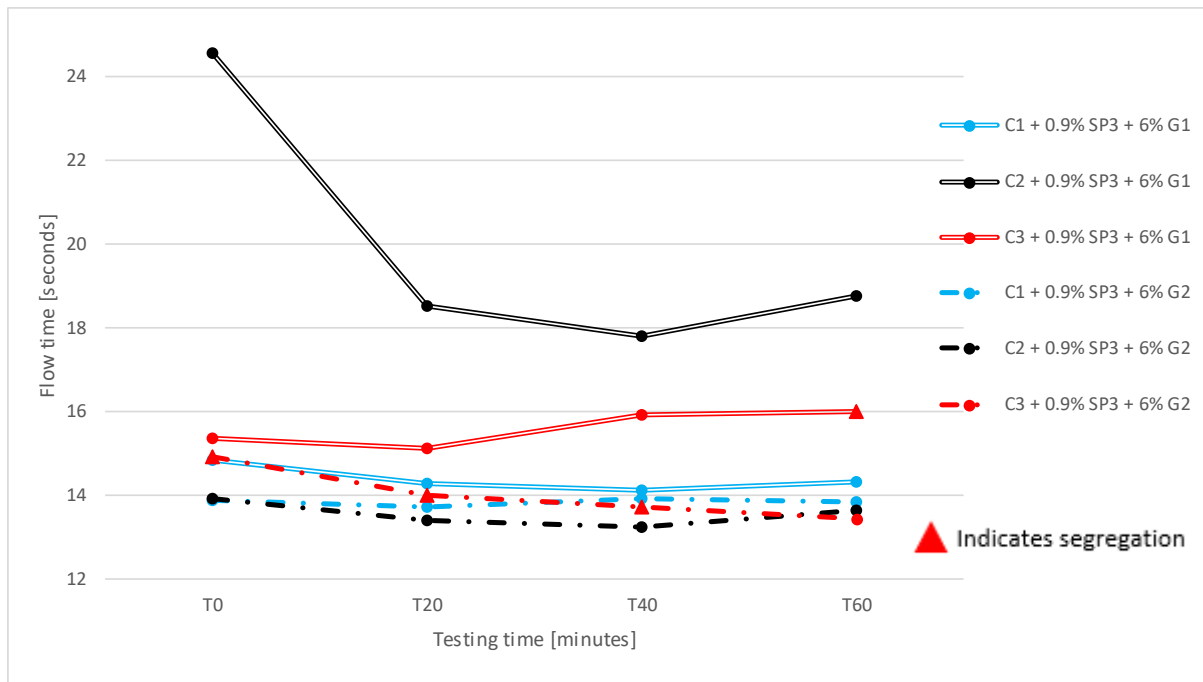


Figure 5.7: Marsh cone test result for different clinkers in combination with 0.9% SP3 and bassanite/gypsum

The addition of SP4 significantly reduced the flowability of C1 as seen in Figure 5.8, to such an extent where the majority of the paste remained in the Marsh cone after testing at times of 20 and 40 minutes, with only a few drops observed at the final testing time, indicating a total loss of flowability as shown in Figure 4.30. Similar flow times measured at T0 and T60 are shown for C2 and C3, with a similar trend when referring to the loss in flowability between testing times of 0 and 20 minutes. C3 exhibited a more drastic increase in flow time where after it decreased again, compared to the gradual loss in flowability for C2.

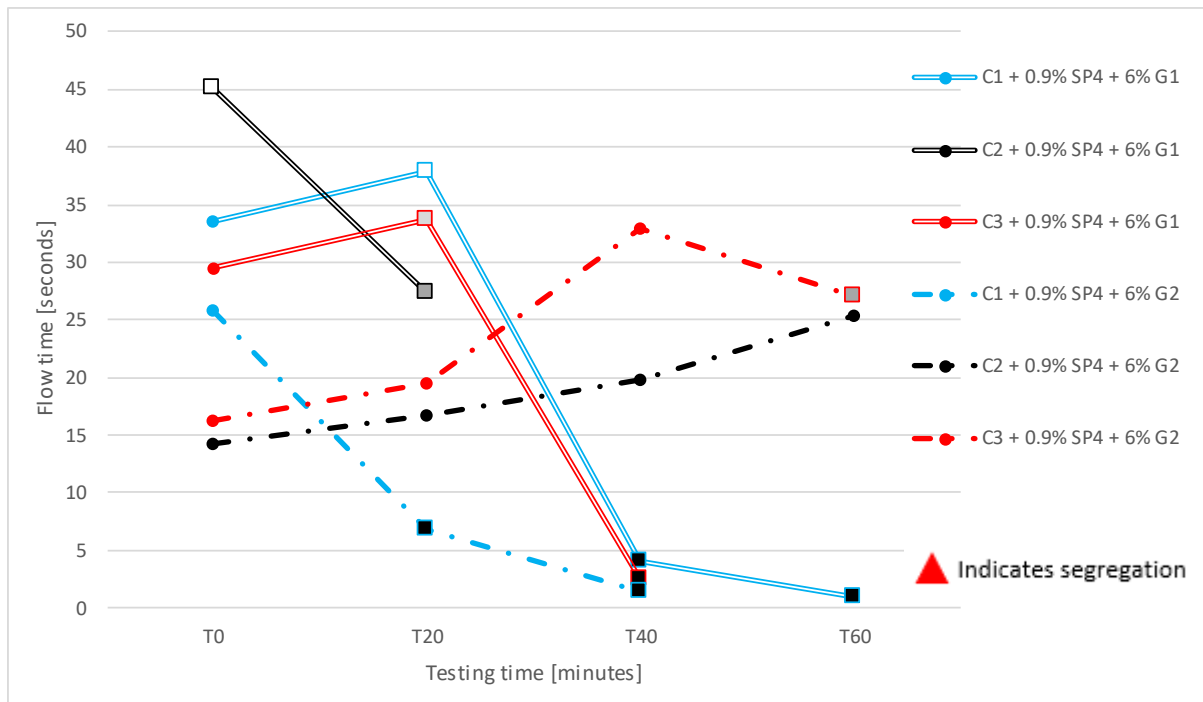


Figure 5.8: Marsh cone test result for different clinkers in combination with 0.9% SP4 and bassanite/gypsum

### 5.1.3. Setting time

Slightly higher setting times occurred for SP2 compared to that of SP1 as shown in Figure 5.9, considering the 6% gypsum addition, with that of C1 being a little higher than C2 and C3, which showed similar setting times. SP3 slightly decreased the setting time of C3 compared to that of SP2, while the overall setting time of C3 decreased a little. The final setting time of C2 is similar when considering SP3 to that observed with SP2, however, the initial setting time decreased. SP4 resulted in a lower setting time for both C2 and C3, as well as the initial set of C1, while the final set of C1 with the addition of SP4 remained similar to that of SP1.

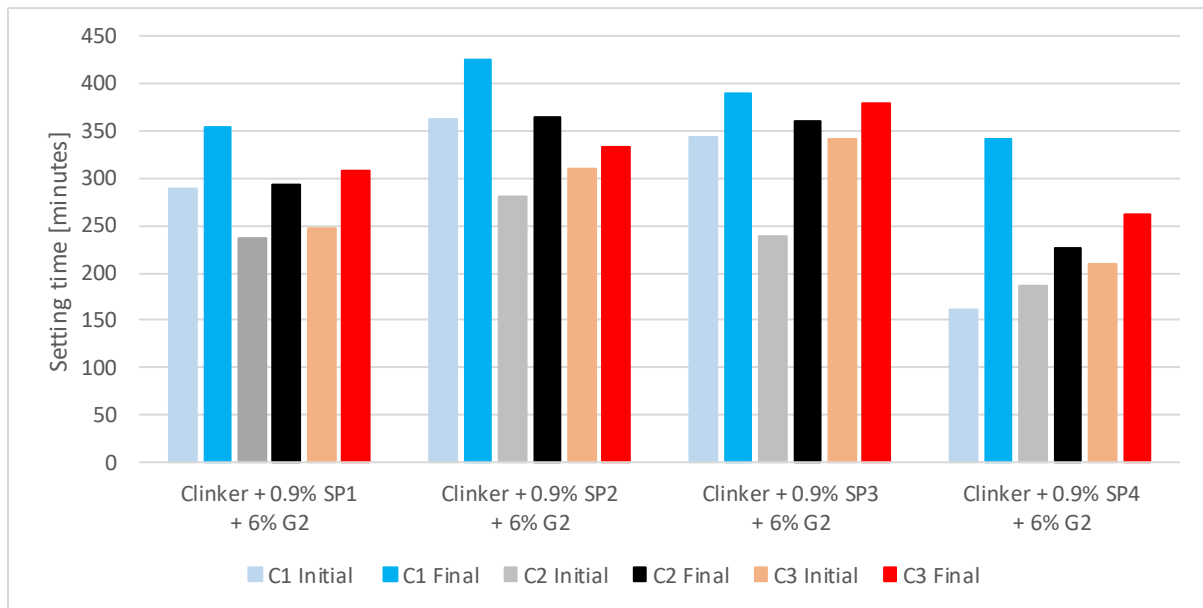


Figure 5.9: Setting time result for different clinkers in combination with 0.9% SP and gypsum

#### 5.1.4. Compression strength

Similar strength gain occurred for SP1, SP2 and SP3 at both the 2- and 7-day testing periods respectively, as seen in Figure 5.10. SP4 resulted in a slight loss of compressive strength for all specimens considered, with the exception being the 2- and 7-day compression strengths of C2 which has a similar result to that of SP3.

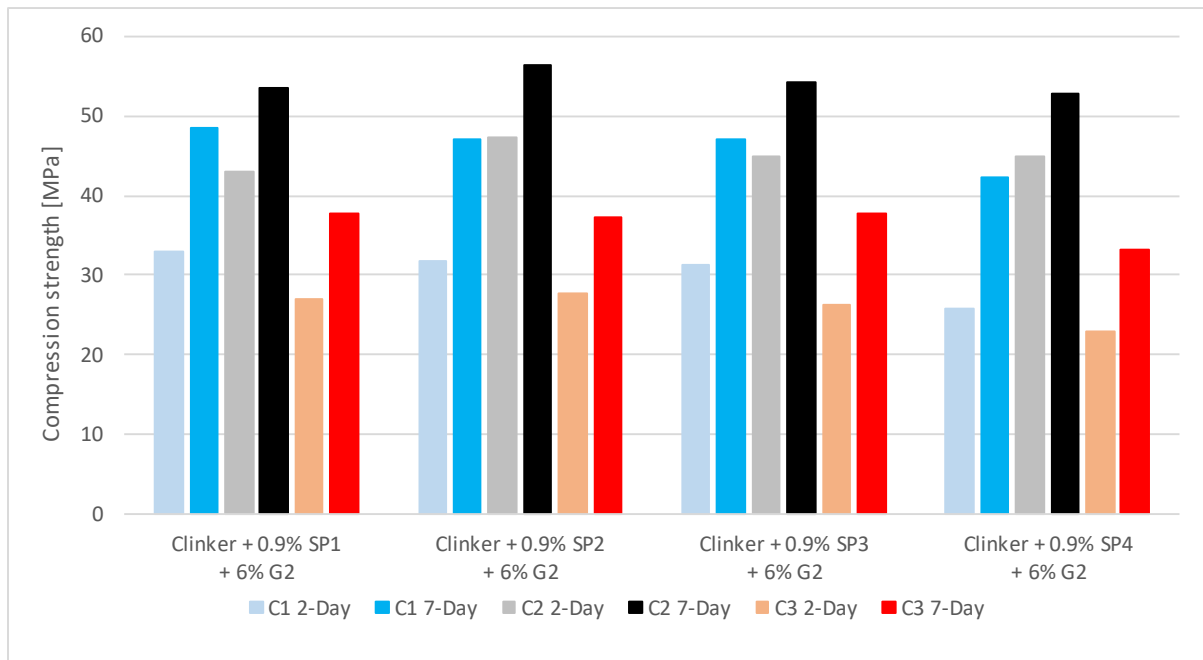


Figure 5.10: Strength test result for different clinkers in combination with 0.9% SP and gypsum

#### 5.1.5. Concluding summary

C3 was more prone to segregation than C1 and C2 when used in combination with 6% gypsum addition. SP4 was the least effective in increasing the flowability of the paste when considering the different mixes in this section. The flowability of the mix containing 6% gypsum addition, significantly reduced for C1 compared to the other clinkers, when considering SP4.

### 5.2. Bassanite and superplasticisers combined

In this section, the addition of bassanite on the effectiveness of the superplasticisers is investigated. Comparing the effects of both a 2% addition and a 6% addition of bassanite will have on the reaction between a high dosage of 0.9% and a low dosage of 0.2% of superplasticiser respectively.

#### 5.2.1. Mini slump

The results obtained for the mixes containing SP1 is shown in Figure 5.11. With the addition of 2% bassanite to the C1 mix with 0.2% SP1, the 0-minute slump flow decreased compared to that without bassanite, and in the time during which mixing stopped to conduct the tests, the mix false set resulting in no slump flow at all. When a 6% addition of bassanite is considered, the slump flow again decreased while no false set occurred. For C3 a decrease in slump flow can be observed, with a lower slump flow measured as the bassanite dosage increased. C2 is the only to show an increase in the measured slump flow with the addition of bassanite. The increase in slump flow is shown to be almost double for the

2% bassanite addition than for that of the 6% bassanite addition, suggesting the optimal bassanite dosage for C2 to be close to that of 2%.

For all of the tests conducted in this section, the slump flow decreased over time, concluding that the superplasticiser lost its effectiveness as time progress. C1 and C3 both resulted in a more rapid loss of workability in the presence of bassanite than without, while the addition of bassanite was found to retard the loss in slump flow of C2.

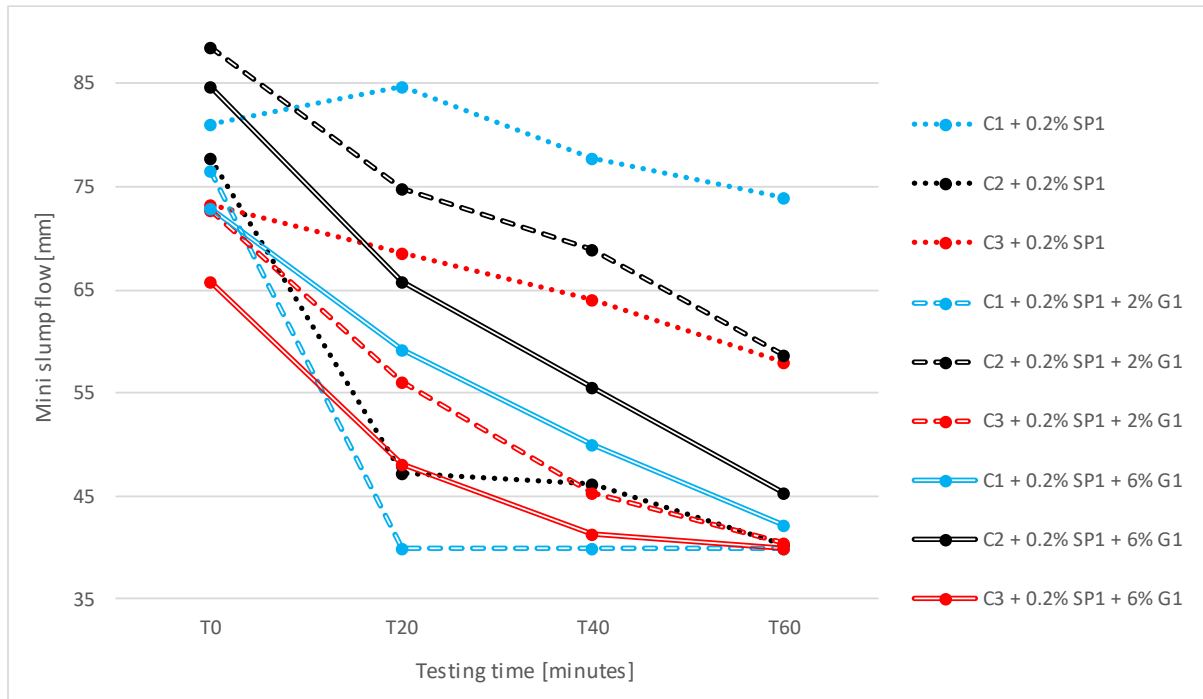


Figure 5.11: Mini slump test result for different clinkers in combination with 0.2% SP1 and bassanite

As shown in Figure 5.12, C1 again resulted in a decreased slump flow with the addition of bassanite, with a bigger loss in slump flow being associated with the larger addition, 6%, of bassanite. However, false set did not occur when considering SP2, unlike previously when SP1 was used. For C3, a similar result occurred with the addition of 2% bassanite to that of only the superplasticiser, but after 20 minutes, the slump flow decreased significantly more rapid with the addition of the bassanite. With 6% bassanite added to the C3/superplasticiser mix, a much lower slump flow resulted, motivating the concept that the bassanite addition reduces the effectiveness of the superplasticiser.

When considering C2, a lower slump flow is also observed with the addition of bassanite, while a steady decrease in slump flow occurred, similar to that of the mixture without any bassanite. With the 2% bassanite addition, a sudden increase in the slump flow occurred at the 40 minute testing time, suggesting in a reaction between the bassanite and superplasticiser.

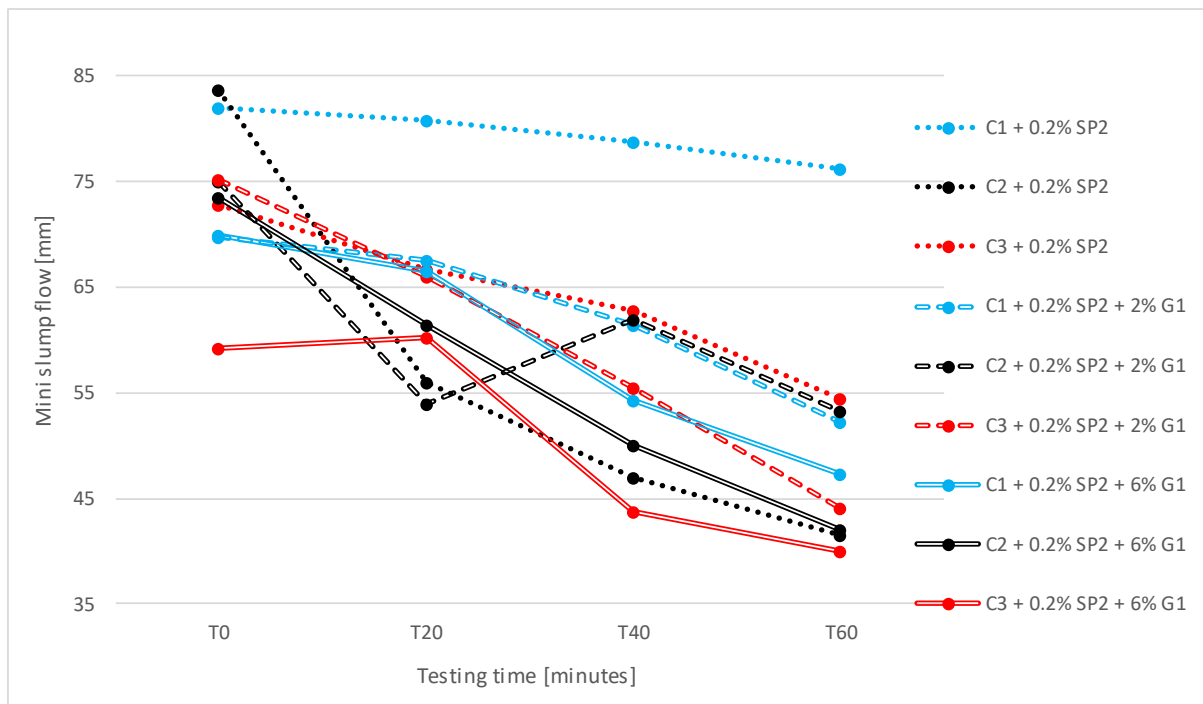


Figure 5.12: Mini slump test result for different clinkers in combination with 0.2% SP2 and bassanite

As seen in Figure 5.13, similar to the results with SP1, false set occurred for C1 with 2% bassanite addition. A lower slump flow also resulted with 6% bassanite added to C1 than without it, however, this decrease in slump flow is much less than that seen in Figure 5.11 with SP1. The slump flow measured for C2 is lower for the mixes containing bassanite at testing time 0 minute, while after 20 minutes, the slump flow increased significantly for the mixes containing bassanite, with the 2% bassanite addition showing to be more effective in aiding the increase in slump flow than that of the 6% addition.

C3 showed to have little effect when adding bassanite to the mix, the slump flow, however, decreased more rapidly after the 40-minute testing time when containing bassanite.

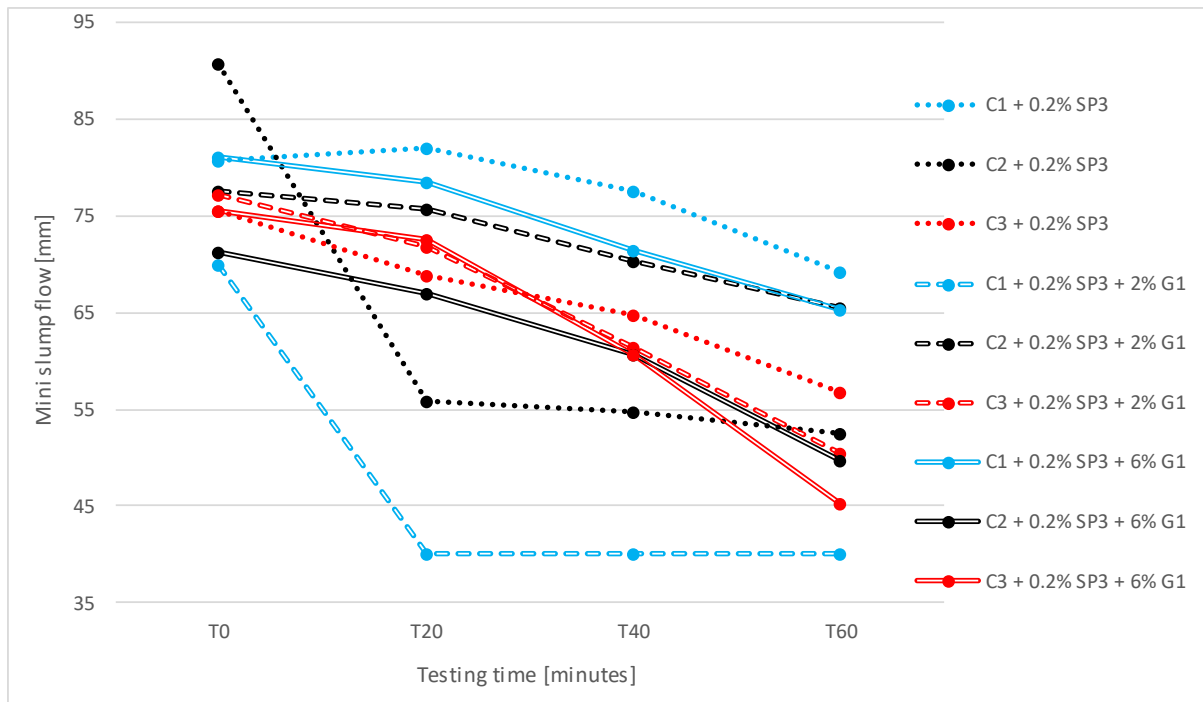


Figure 5.13: Mini slump test result for different clinkers in combination with 0.2% SP3 and bassanite

In Figure 5.14 the results are shown when 0.2% SP4 is combined with bassanite. For C1, a lower 0-minute slump flow is shown with the addition of 2% bassanite, with false set again occurring during the initial testing phase. When adding 6% bassanite, the same T0 slump flow occurred as when no bassanite is added, however, the slump flow decreased rapidly over time when bassanite is added. Without any bassanite addition, C2 showed a high slump flow when measured at 0 minutes, which then decreased to zero at 20 minutes. With a 2% bassanite addition, the 0-minute slump flow is not as high as that measured without the bassanite addition but similarly decreased after the 0 minute testing time. The 2% addition did however not reach the zero-slump flow, instead increasing again after the 20 minute testing time. When adding 6% bassanite to C2, a low initial slump flow resulted, which steadily decreased with time.

C3 resulted in an increased slump flow with the addition of 2% bassanite, gradually decreasing over time while a decrease in slump flow resulted with 6% bassanite addition, this mix also gradually decreased in slump flow as time passed, to reach a point of zero slump flow for all three cases at the 60 minute testing time for C3.

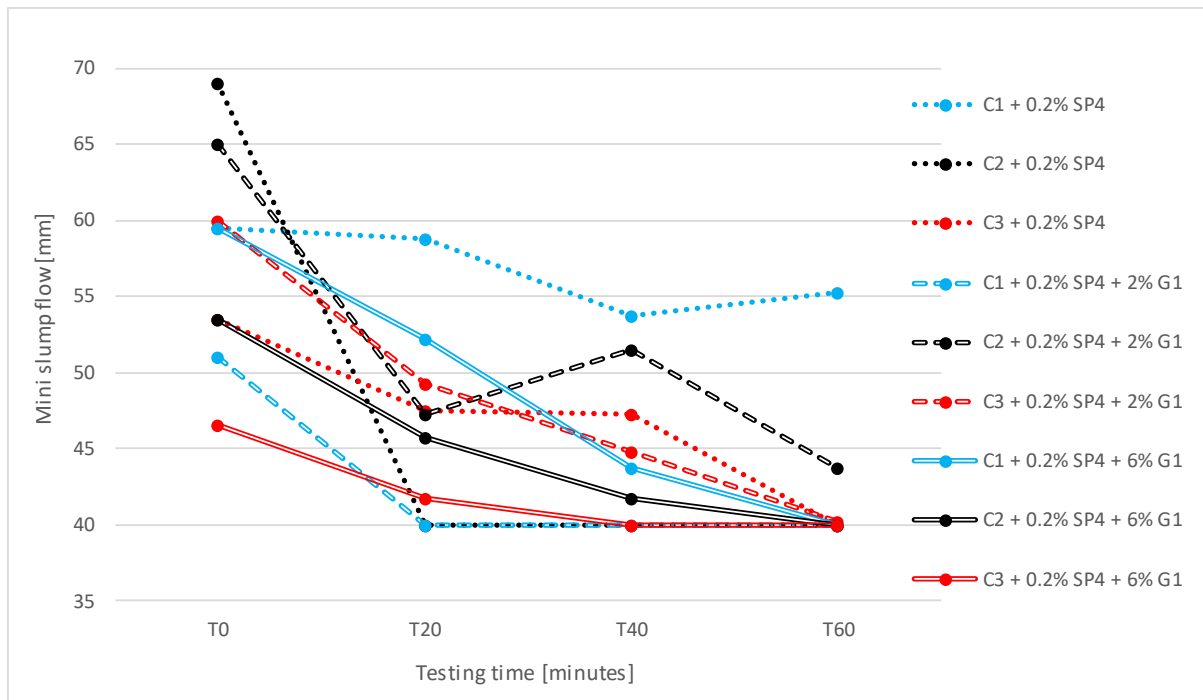


Figure 5.14: Mini slump test result for different clinkers in combination with 0.2% SP4 and bassanite

At 0.9% dosage SP1 seen in Figure 5.15, C3 with high  $C_2S$  and  $C_3A$  content, medium  $C_4AF$  and low  $C_3S$ , showed the smallest increase in slump flow, gradually decreasing over time. With the addition of 2% bassanite, the 0-minute slump flow is shown to be higher, increasing over the 20 minutes mixing time where after it stayed nearly constant. After an hour of mixing, the slump flow decreased significantly, suggesting the superplasticiser may have become ineffective at that time. The addition of 6% bassanite increased the slump flow of the mixture. At the 20 and 40 minute testing times similar results are obtained, suggesting the increased slump flow is maintained by the 6% bassanite addition.

C1, with high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content showed a higher 0-minute slump flow with the addition of 2% bassanite, although this addition caused an acceleration in the decrease in slump flow. The 6% addition of bassanite showed a larger influence on the increase in slump flow than the 6% addition of gypsum, which decreased over time, unlike the bassanite.

C2 with a high  $C_3S$  and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content showed similar results for all mixes considered in this section at testing time 0 minutes, as seen in Figure 5.15. With the addition of 2% and 6% bassanite, as well as 6% gypsum, the results remained fairly constant throughout the testing period, however, when no bassanite/gypsum is present, the slump flow decreased over time.



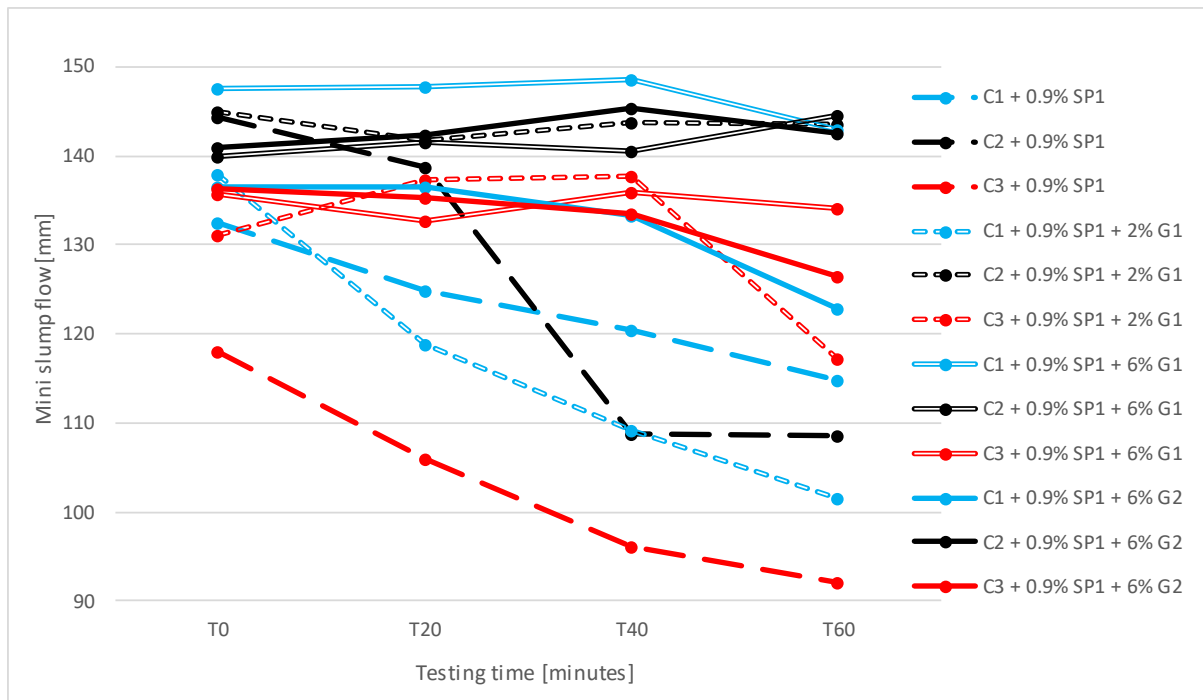


Figure 5.15: Mini slump test result for different clinkers in combination with 0.9% SP1 and bassanite/gypsum

Considering 0.9% SP2 in Figure 5.16 the following observations can be made. For C1 a much higher 0-minute slump flow resulted when adding 2% bassanite to the mixture, over time this addition showed to cause a drastic drop in slump flow after the T0 testing time and then continuing to decrease with time. When adding 6% bassanite, a lower 0-minute slump flow occurred but this increased with time, resulting in the highest slump flow measured at 60 minutes. Comparing this to the 6% gypsum addition which showed a slight increase in the 0-minute slump flow when compared to the reference 0.9% superplasticiser mix, which decreased steadily over time.

For both the 2% bassanite addition as well as the 6% gypsum addition used in combination with C2, the 0-minute slump flow is lower than that of the reference 0.9% SP2 mix. However, unlike the reference mix, the slump flow increased over time for both these mixes, reaching similar results as testing continued with time. When adding 6% bassanite to the reference mix, a significant decrease in slump flow occurred at T0 testing time. Although the slump flow increased over time, it still showed to have lower values compared to the other additions.

C3 showed an increase in slump flow for all additions considered as seen in Figure 5.16. 2% bassanite addition increased the 0-minute slump flow while maintaining a slight increase over time. The 6% bassanite caused an initial drop in slump flow while 6% gypsum increased the 0-minute slump flow slightly. The effect of the gypsum remained fairly constant throughout the testing time, with the 6%

bassanite increasing the slump flow from the 0-minute measured value, striving towards the result obtained when considering the gypsum mix, as time passes.

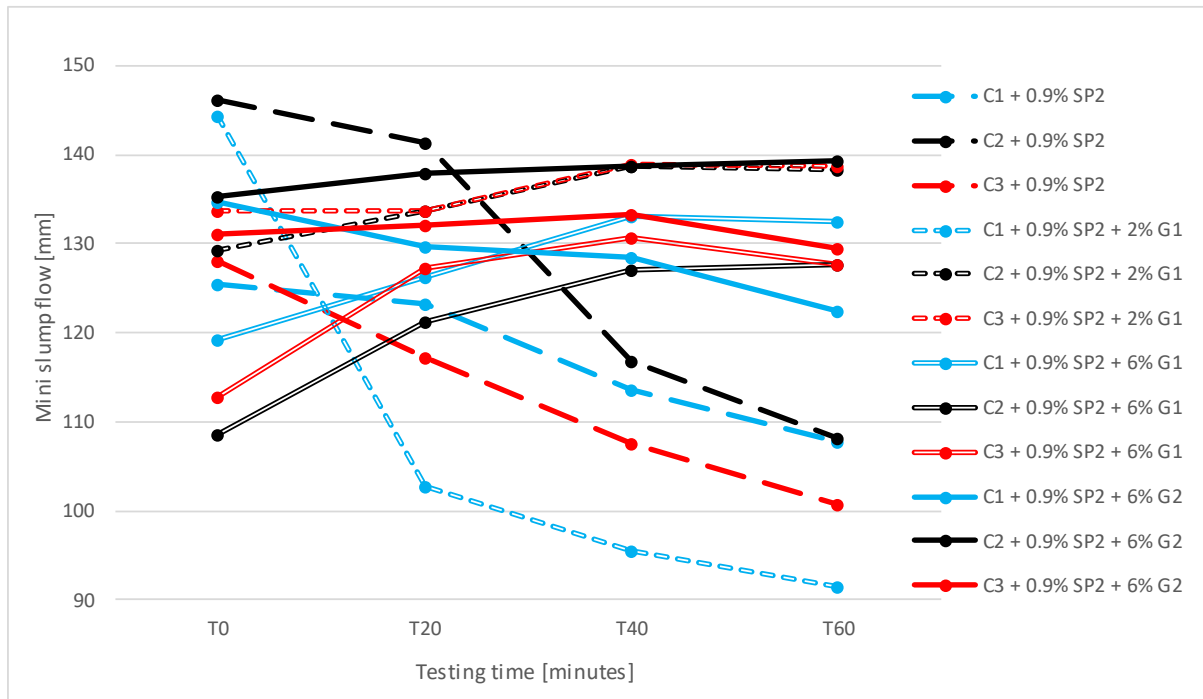


Figure 5.16: Mini slump test result for different clinkers in combination with 0.9% SP2 and bassanite/gypsum

With 0.9% SP3 in Figure 5.17, C2 with a high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content showed the highest increase in the 0-minute slump flow measured. With the addition of 2% bassanite, a lower slump flow resulted which stayed constant throughout the testing procedure. The addition of 6% gypsum only slightly decreased the 0-minute slump flow, however, the slump flow steadily decreased with time reaching values of that similar to when the 2% bassanite addition is considered. A much lower slump flow resulted when 6% bassanite is used but as time progressed, the slump flow increased significantly, suggesting a delay in reaction time between the superplasticiser and the cement/bassanite.

The addition of 2% bassanite and 6% gypsum reacted similarly when considering the effect on C3, showed in Figure 5.17. It can be noted that at the last testing of time = 60 minutes, the mix with the gypsum addition still maintained the increased slump flow while the slump flow of the 2% bassanite mix started to decrease. Although still significant, the 6% addition of bassanite increased the slump flow to a lesser extent than the other additions, increasing slightly over time to reach a similar result than the 6% addition of gypsum at time of 60 minutes. This could indicate 6% gypsum and 6%

bassanite having the same impact on the slump flow of the mix, with the reaction between the bassanite and superplasticiser taking longer than that of the gypsum and the superplasticiser.

A 2% addition of bassanite resulted in a significant increase in the initial slump flow for C1 where after the slump flow significantly decreased in the first 20 minutes after the 0 minutes testing and then more gradually afterwards. The addition of 6% bassanite showed the smallest increase in slump flow initially, however, over time the measured slump flow kept increasing. The opposite occurred for the 6% gypsum addition where a bigger increase in initial slump flow resulted, but which decreased over time.

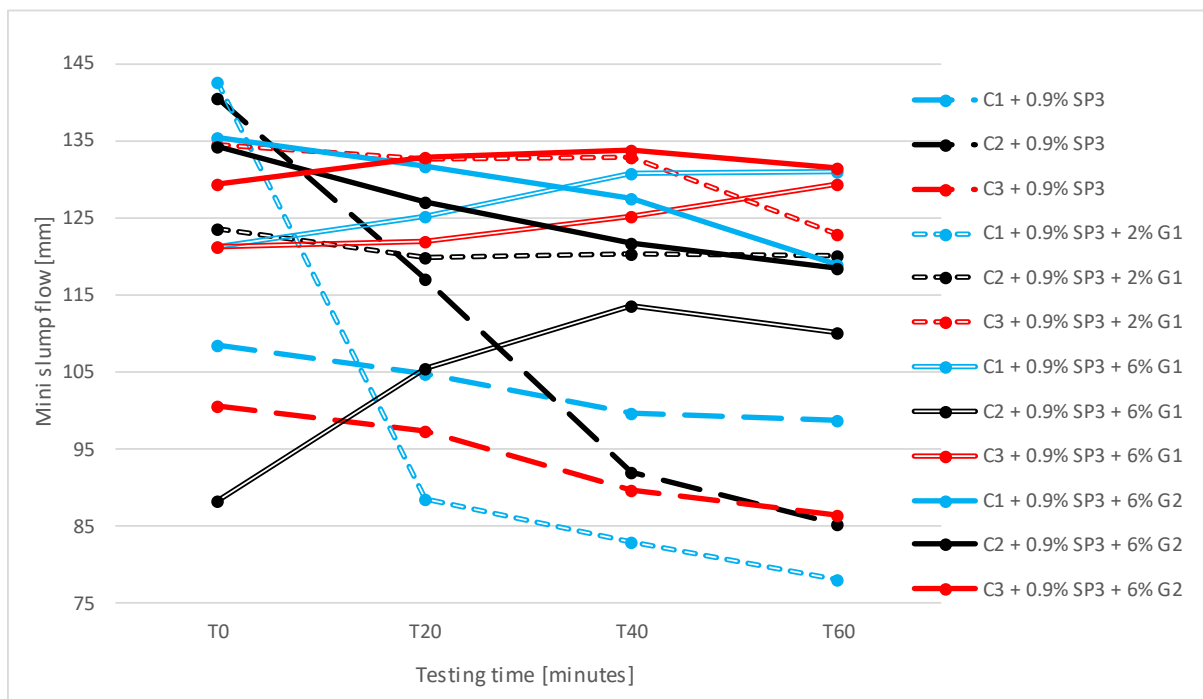


Figure 5.17: Mini slump test result for different clinkers in combination with 0.9% SP3 and bassanite/gypsum

Figure 5.18 showed a fairly constant slump flow over time at 0.9% SP4 dosage for C1. When adding 2%- and 6% bassanite as well as 6% gypsum, similar results are shown. These additions increased the 0-minute slump flow but decreased over time. With the 2% bassanite and 6% gypsum additions showing a significant decrease in slump flow between time 0 and 20 minutes, while the loss in slump flow is more gradually for the 6% bassanite addition, suggesting it takes longer to react with the other materials.

C2 is found to be most effective when considering 0.9% SP4, with similar results being obtained when adding 6% gypsum to the mix, as shown in Figure 5.18. For 2% addition of bassanite, a decrease in

slump flow occurred while this decrease was even bigger for the 6% bassanite addition. For all the mixes containing C2, the slump flow gradually decreased over time.

C3 with high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  contents, shows a higher 0-minute slump flow when adding 2% and 6% bassanite, but these values decrease with time to give slump flows similar to that of the reference mix, containing only 0.9% superplasticiser, at the other times of testing. When considering the 6% gypsum addition, the slump flow increased significantly for all times during the testing period, decreasing with a nearly constant gradient over time.

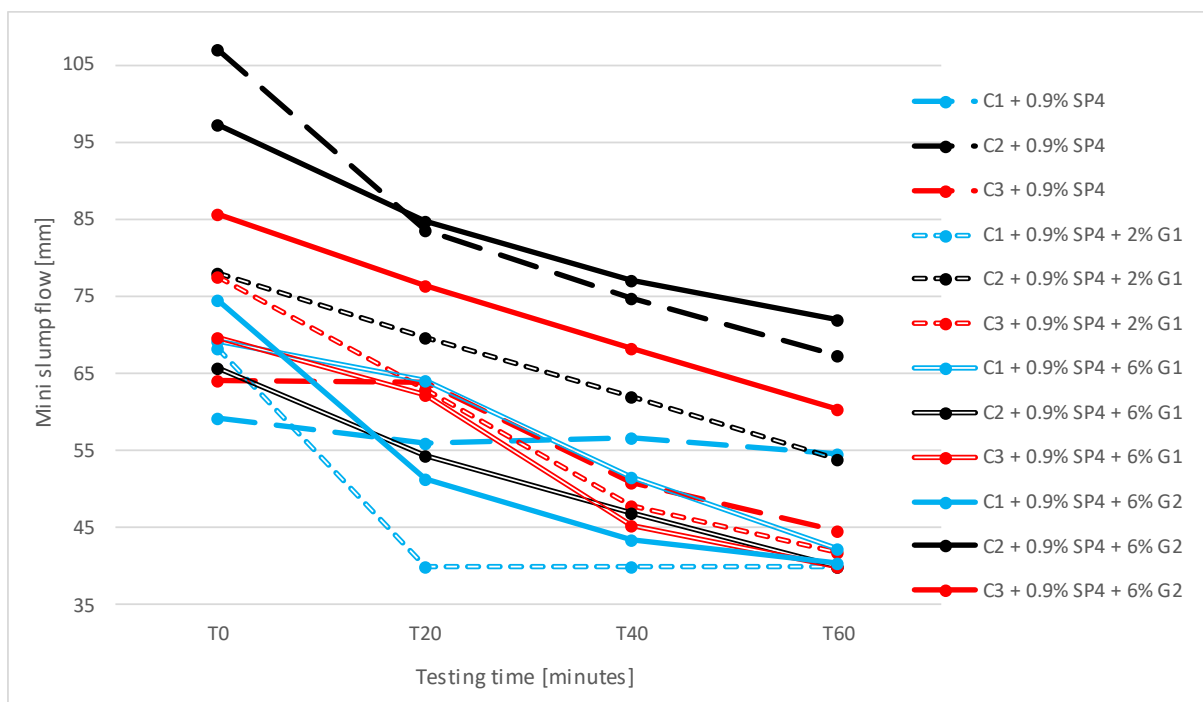


Figure 5.18: Mini slump test result for different clinkers in combination with 0.9% SP4 and bassanite/gypsum

The mini slump test results in Figures 5.15 to 5.18, combining superplasticiser with the additions of gypsum, confirms Ramachandran et al. (1989) who claims that the measured slump values of concrete containing only superplasticiser is lower than that of concrete containing both superplasticiser together with a higher gypsum content.

### 5.2.2. Marsh Cone

As seen in Figure 5.19, C1 with high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content, showed fairly constant results for the reference. With the addition of 2% bassanite, the 0 minute flow time increased by 18 seconds indicating a much lower flowability. After the 0 minute testing time, the mixture false

set and no further testing was possible on this mix. With the addition of 6% bassanite, a decrease in flowability was again observed, with paste remaining in the Marsh cone after all times of testing.

For C2, the addition of 2% bassanite increased the flowability of the mixture at all times of testing, improving the results at 20 and 60 minutes to run empty, where at the reference mix, 70% and 97% paste remained respectively and improving on the few drops measured at 60 minutes to where only approximately 27% of the paste remained in the Marsh cone after testing. The 6% addition of bassanite decreased the flowability of the mix initially but decreased the amount of paste left over in the cone at testing times 20 and 60 minutes, while similar results to that of the reference mix were obtained at 60 minutes where only a few drops existed the cone.

For C3 both the 2% - and the 6% bassanite addition decreased the flowability severely as no test was able to empty the Marsh cone. The larger addition of 6% bassanite decreased the flowability more than that of the 2% bassanite addition.

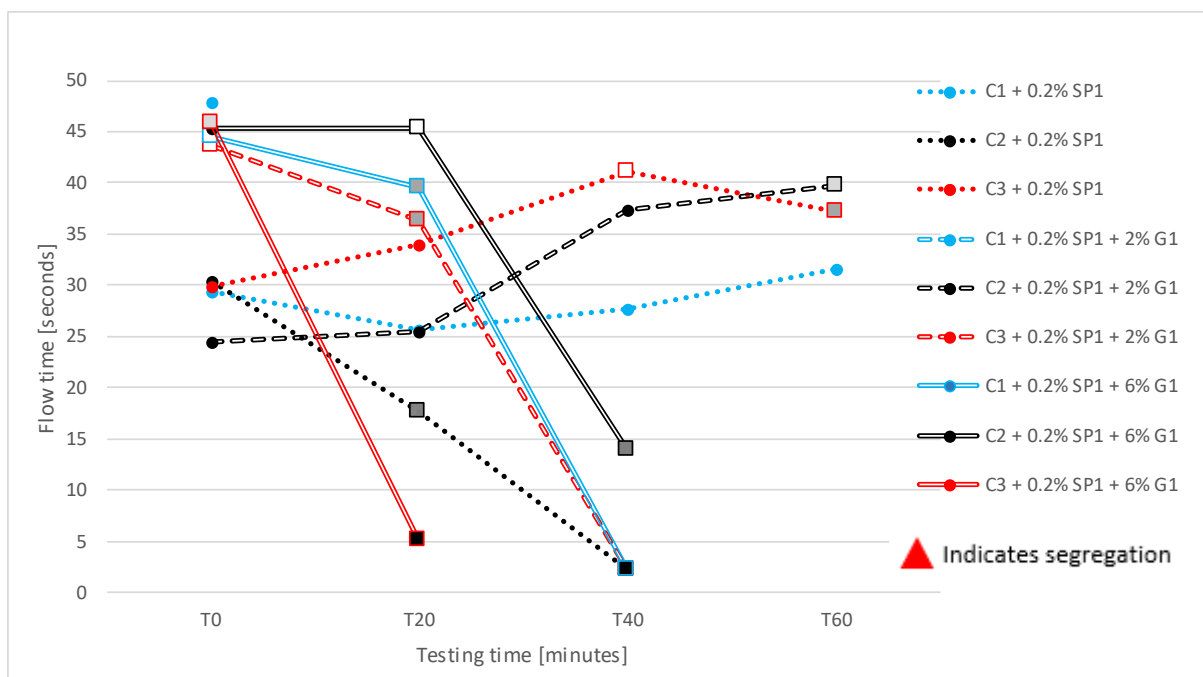


Figure 5.19: Marsh cone test result for different clinkers in combination with 0.2% SP1 and bassanite

In combination with 0.2% SP2 as shown in Figure 5.20, a 2% addition of bassanite to the reference mix of C1 showed similar results than that of 0.2% SP1, where the 0 minute flow time was increased, where after false set of the mix occurred. For SP2 the flow time increased by only six seconds compared to the 18 seconds found when using SP1. For a 6% addition of bassanite, the flowability of the mix initially

and at testing time of 20 minutes decreased with some of the paste remaining in the cone after testing at times of 40- and 60 minutes, unlike the reference mix where testing at all times gave a clean result.

For C2, the addition of 2% bassanite seemed to improve the flowability of the mix overall, despite having an increased flow time initially. At testing time of 20 minutes, the bassanite addition resulted in a clean result where for the reference mix, containing only superplasticiser, some paste remained in the cone. A smaller percentage of mixture remained in the cone at testing times of 40- and 60 minutes. When considering the 6% bassanite addition the flowability of the mix decreased, leaving paste remaining in the cone for all testing times. For this addition, the time of continuous flow was longer than that of the reference mix with a smaller percentage of paste remaining in the Marsh cone. This possibly suggests that the particle shape and/or size of the bassanite improves the flowability of the mixture while the chemical properties of the addition interact with the clinker to lessen the effect of the superplasticiser.

For C3 with the addition of 2% bassanite, similar results are shown both initially and for the other testing times considered, than for the reference mix. However, more paste remained in the cone with the bassanite addition than for the reference mix at both testing times of 40- and 60 minutes respectively. The 6% addition of bassanite decreased the flowability of the paste significantly without any test being able to run clean. Unlike C2 where a longer continuous flow time could be measured with less paste remaining in the cone, a short flow time and a larger percentage of paste remained in the cone for C3, with high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  contents.

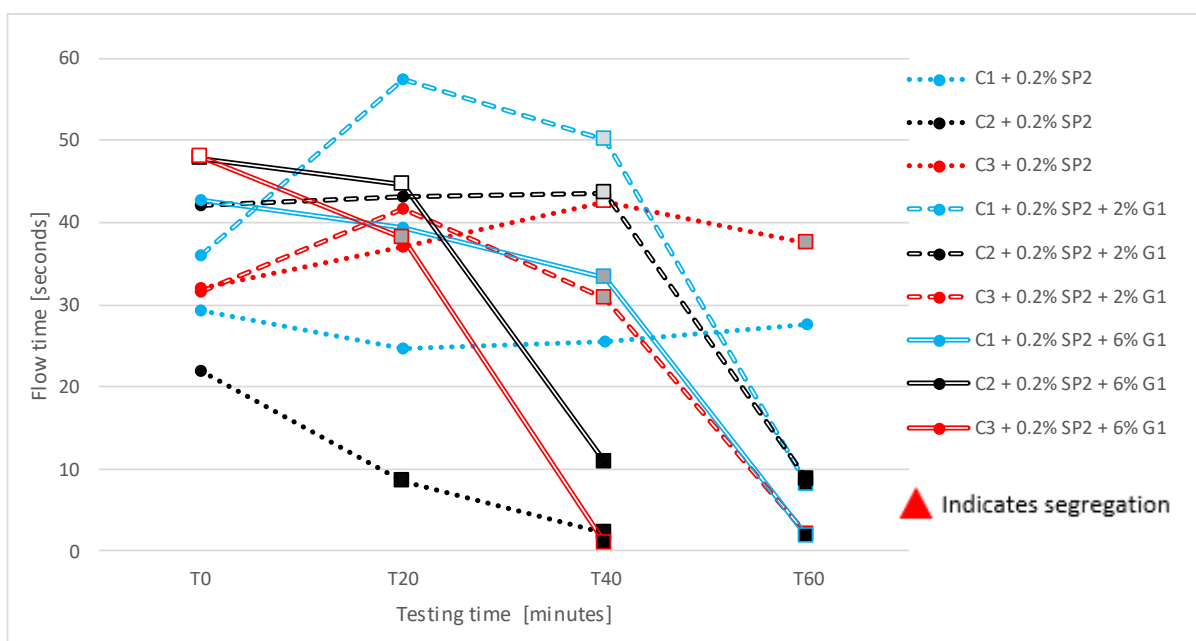


Figure 5.20: Marsh cone test result for different clinkers in combination with 0.2% SP2 and bassanite

As seen in Figure 5.21, for C1, false set again took place with the 2% addition of bassanite, with the 0 minute flow time being increased by only three seconds, compared to the 18 and 6 seconds observed for SP1 and SP2 respectively. For the 6% bassanite addition a decrease in flow time occurred, relating to the increased flowability of the mix, which was not the case for any other mix considered thus far.

The addition of 2% bassanite was found to increase the flowability of the mix containing C2, for testing times 20-, 40- and 60 minutes, as seen in Figure 5.21, rather drastically, while the 0 minute flow time was measured to be slightly longer for the reference mix containing only superplasticiser. The 6% bassanite addition decreased the flowability of the mix, with no clean test result being noted for this addition.

C3 showed a slight overall increase in flowability with the addition of 2% bassanite, while similar results to that of the reference mix were obtained for the addition of 6% bassanite. The bassanite additions did not seem to have much of an influence on the flowability of the C3 mixes in combination with the 0.2% SP3 dosage.

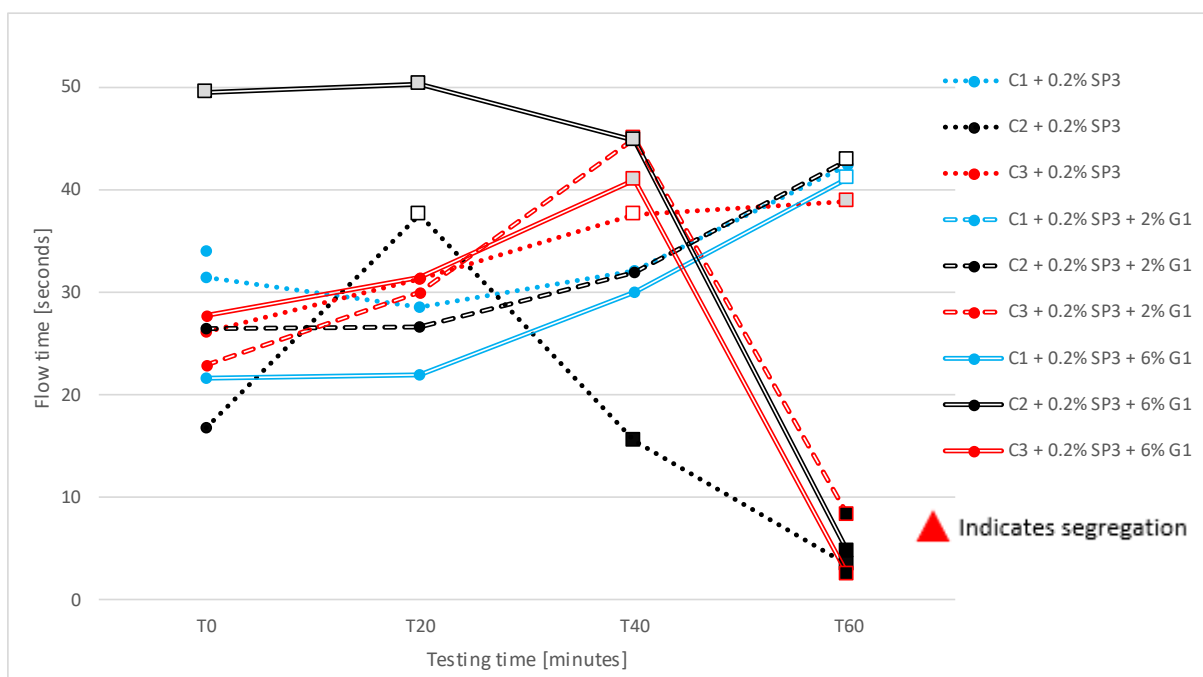


Figure 5.21: Marsh cone test result for different clinkers in combination with 0.2% SP3 and bassanite

Considering the 0.2% SP4 dosage, for C1, the addition of 2% bassanite caused the continuous flow to stop much faster than for the reference mix containing only superplasticiser, with a larger percentage of paste remaining in the cone as shown in Figure 5.22. After the 0-minute testing, as with the other

superplasticisers, false set took place. Similar results to that of the reference mix are shown for the 6% bassanite addition, where neither of the tests ran clear during the testing period.

Initially, for C2, the 2% bassanite addition decreased the flowability of the mix by increasing the flow time as well as causing roughly 5% of the paste to remain in the Marsh cone. Over time, however, this addition increased the flowability of the mix to where only a few drops and then no drops were measured at testing times of 40 and 60 minutes, to 75% and 96% remaining respectively. The 6% bassanite addition significantly decreased the flowability of the mixture from where the reference mix emptied the cone to only 10% of the paste passing through the cone, where after only a few drops were observed at the other testing times.

For C3 the 2% bassanite addition affected the 0-minute flowability of the mix from where around 40% of the reference mix passed through the cone in 25 seconds before the flow ceased, to where 70% of the mix passed through the cone in 40 seconds before the continuous flow stopped. For the other testing times, similar results are shown to that of the reference mix. With the 6% addition of bassanite, the flowability of the paste decreased to where the 0-minute testing time continuous flow lasted for only five seconds, leaving roughly 84% of the paste remaining in the cone. For the other testing times considered, only around 2% of the paste existed the cone at testing time of 20 minutes, while only a few drops for the other times of testing.

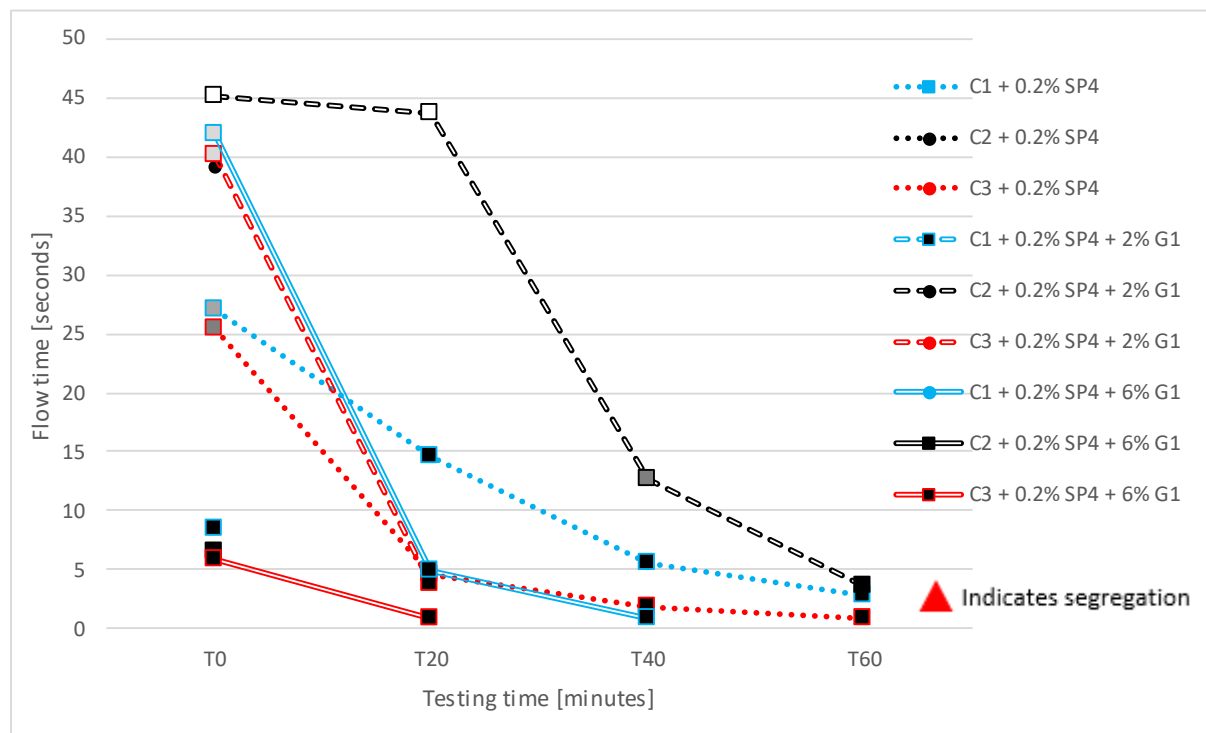


Figure 5.22: Marsh cone test result for different clinkers in combination with 0.2% SP4 and bassanite



For C1, the addition of 2% bassanite to the mix containing 0.9% SP1, decrease in flow time was noted with the mixture segregating at the 0 minute testing time, as shown in Figure 5.23. Over time, the segregation of the mix stopped with the flow time measured at the various testing times being higher than that of the reference mix containing only superplasticiser. The addition of 6% bassanite resulted in a decrease in flow time, which remained constant over the testing period, with segregation of the mix occurring at all stages. Adding 6% gypsum increased the flowability even more than the addition of 6% bassanite, also remaining constant over the testing period. For the gypsum addition, segregation occurred at testing times 0 and 20 minutes, however, segregation stopped when measuring at times of 40 and 60 minutes, unlike the results obtained for the 6% bassanite addition.

Considering C2, similarly to the reference mix, the mix segregated only at the 0 minute testing time for the 2% bassanite addition. This addition decreased the flowability of the paste over the testing period. For both the 6% bassanite and 6% gypsum additions, segregation occurred at all four testing stages. The 6% gypsum addition increased the 0-minute flowability of the mixture slightly more than that of the 6% bassanite addition while remaining to increase the flowability over time. The bassanite addition, on the other hand, resulted in a constant flowability measured over time.

When used in combination with C3, the addition of 2% bassanite increased the flowability of the mixture. This increase remained constant over the testing period with similar flow times measured at all times. Segregation occurred at the first three testing times after which, at testing time of 60 minutes, the segregating of the mixture ceased. For both the 6% bassanite and 6% gypsum addition, segregation occurred at all testing times. The 6% bassanite addition increased the flowability of the mix to a lesser extent than that of the 2% bassanite addition, while the 6% gypsum addition improved the flowability more than that of the 2% bassanite addition.

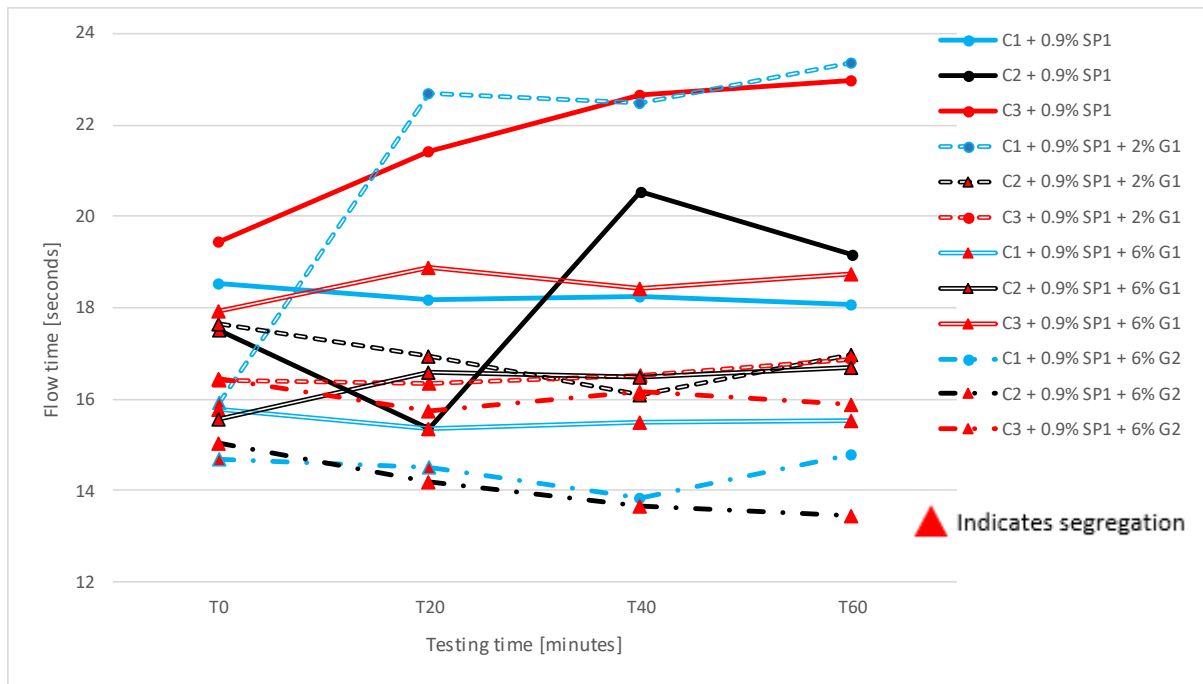


Figure 5.23: Marsh cone test result for different clinkers in combination with 0.9% SP1 and bassanite/gypsum

For C1 as shown in Figure 5.24, with the addition of 2% bassanite, the 0 minute flow time of the mix decreased in comparison to that of the reference mix containing only superplasticiser, while segregation of the paste occurred. Testing at the other times considered, the flowability decreased compared to that of the initial results, having a higher flow time than the reference mix at those times. The addition of 6% bassanite decreased the 0 minute flow time to a similar value than the 2% addition. At testing time of 20 minutes, the flow time decreased even more but started to slightly increase over time from there. The 6% gypsum addition resulted in the highest increase in flowability and maintained a constant flow time over the testing period.

Segregation occurred for the reference mix containing C2 at testing times 0- and 20 minutes, however with the additions considered, no segregation occurred. For the 2% and 6% bassanite additions, similar results are shown, with similar flow times being measured at testing time 0 minutes. For both these additions, the flow times decreased similarly at the testing time of 20 minutes and then remained constant throughout the testing procedure. For the 6% gypsum, however, a much lower 0-minute flow time can be observed, slightly decreasing over time for the period considered during testing.

Figure 5.24 showed for C3, the 0 minute testing time result of the reference mix segregated, the addition of the 6% bassanite eliminated the initial segregation while both the 2% bassanite and 6% gypsum additions resulted in segregation at all testing times considered. While the 2% bassanite addition resulted in the biggest increase in flowability, it slightly decreased over time. The 6%

bassanite and 6% gypsum additions resulted in similar 0 minute flow times, while these remained similar for the 6% gypsum addition over time, the 6% bassanite addition resulted in an even bigger increase in flowability at 20 minutes with the flow times increasing slightly from there as time progressed.

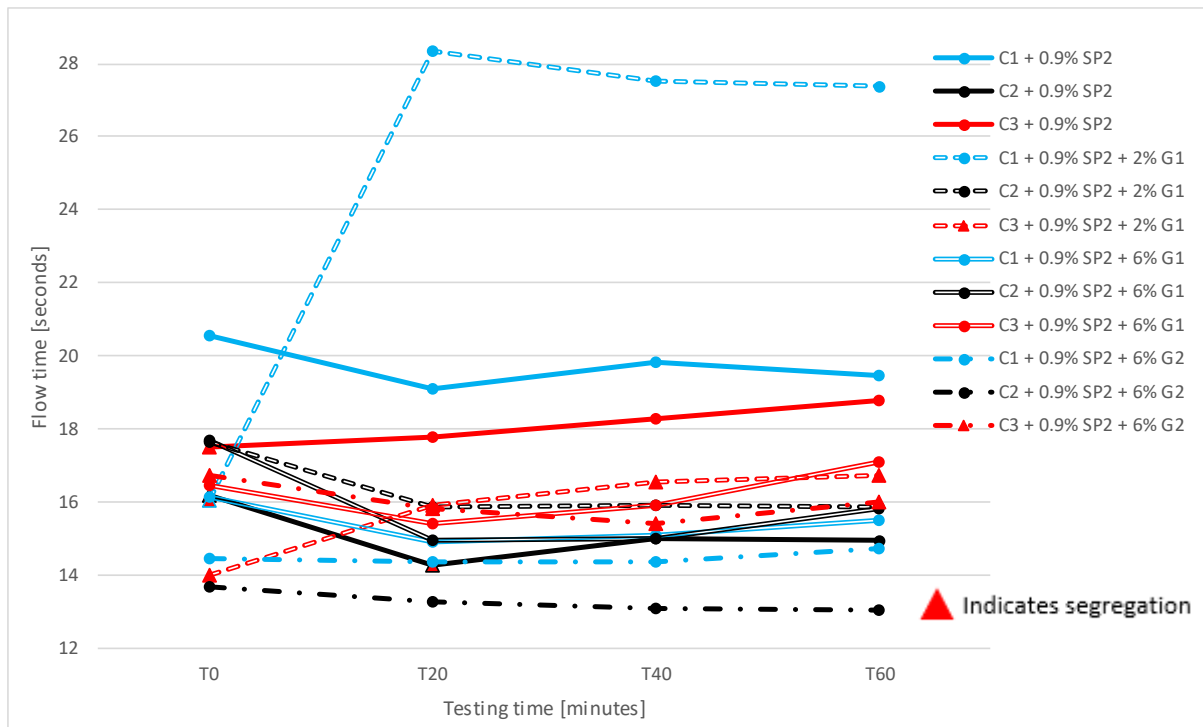


Figure 5.24: Marsh cone test result for different clinkers in combination with 0.9% SP2 and bassanite/gypsum

For C1 as shown in Figure 5.25, at 0-minute testing, the mixture segregated with the addition of 2% bassanite where after the flow times increased significantly compared to that of the reference mix containing only superplasticiser. Both the 6% bassanite, as well as the 6% gypsum additions, increased the flowability of the mixture resulting in a reduced, fairly constant, flow time for all testing times considered. The 6% gypsum addition increased the flowability slightly more than that of the 6% bassanite addition.

Segregation occurred at the 0-minute testing for the reference mix containing C2, this was however eliminated by all of the additions considered. The addition of 6% gypsum to the mix resulted in the similar flowability to that of the 0-minute reference mix, with the flow time remaining constant over time. The 2% addition of bassanite increased the 0 minute flow time slightly, with the mixture gaining flowability over time up to the testing time of 60 minutes where a slight decrease can be noted, suggesting the superplasticiser reacted with the components in the mixture for almost an hour before

the reaction started to lose its effectiveness. The 6% addition of bassanite resulted in a much higher 0 minute flow time, again – similarly to that of the 2% addition, the mix slowly increased in flowability over time up to the testing time of 60 minutes where a slight decrease in the flowability occurred.

For C3 no segregation occurred for the reference mix while the additions considered all resulted in some segregation. The 2% bassanite, as well as the 6% gypsum addition, caused segregation at testing times of 0-, 20- and 40 minutes while the 6% bassanite addition only resulted in segregation at the testing time of 60 minutes. The 2% bassanite increased the 0-minute flowability of the paste more than the other additions, however at the testing time of 20 minutes, this flowability decreased again slightly where after the flow time again decreased. The 6% gypsum shows the second biggest improvement on the flowability of the paste, with the flowability constantly increasing over the testing period. The 6% bassanite addition improved the flowability of the mixture by the least amount, continuing to improve the flowability at testing time of 20 minutes whereafter the flow time started to increase again.

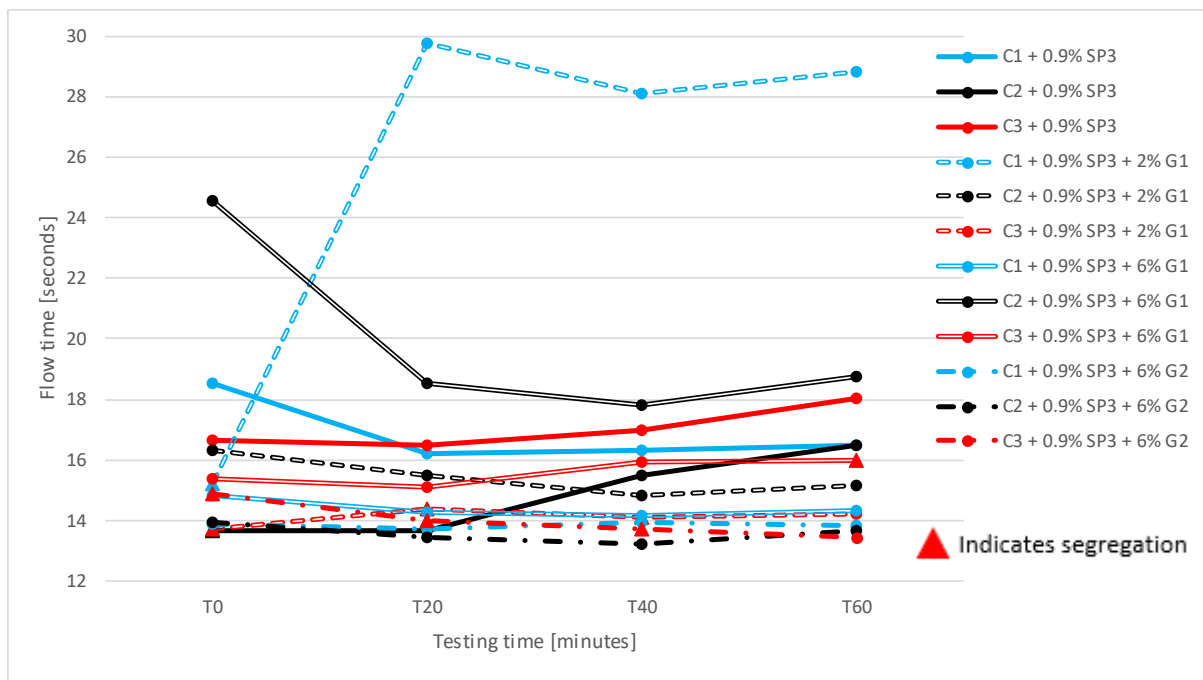


Figure 5.25: Marsh cone test result for different clinkers in combination with 0.9% SP3 and bassanite/gypsum

Considering the 0.9% SP4 addition shown in Figure 5.26, for C1, the 2% addition of bassanite decreased the 0-minute flowability of the mix and resulted in the false set of the mixture after the initial testing time. The 6% addition bassanite improved the 0-minute flowability of the mix to give a clean result, unlike the reference mix at this stage, while the 6% gypsum addition improved the 0-minute

flowability, even more, resulting in a flow time that is 7 seconds faster than that measured with the 6% bassanite addition. At the other testing times, both the 6% additions resulted in paste remaining in the cone after testing. For the bassanite addition, at testing time of 20 minutes, the continuous flow lasted for 38 seconds with only about 7% of the paste remaining in the cone, while for the gypsum addition, the continuous flow stopped after only 7 seconds with nearly 80% of the paste remaining in the cone. Similar results were obtained for these two additions at the other testing times considered.

For C2, seen in Figure 5.26, the 6% gypsum addition increased the overall flow times of the mixture slightly while still maintaining a clean result, as for the reference mix. A significant decrease in flowability occurred for the 6% bassanite addition where not one of the tests gave a clean result for all the testing times considered. The 2% bassanite addition also decreased the flowability of the paste but to a smaller extent than the 6% addition. A much higher flow time was measured for this addition at times 0 and 20 minutes compared to that of the reference mix, while 7% and 75% of the paste remained in the Marsh cone at times of 40- and 60 minutes respectively.

Considering C3, the 6% addition of gypsum showed to have the biggest effect on the increase of flowability. Although the increase in flowability decreased over time, this addition gave clean results for the first three testing times, unlike the reference mix where no clean result was obtained. Initially, clean results also occurred for the 2% and 6% bassanite additions, with the 2% addition having a flow time of five seconds faster than that of the 6% addition. At the various other testing times, these two additions showed similar effects on the flowability of the mix with paste remaining in the cone after testing.

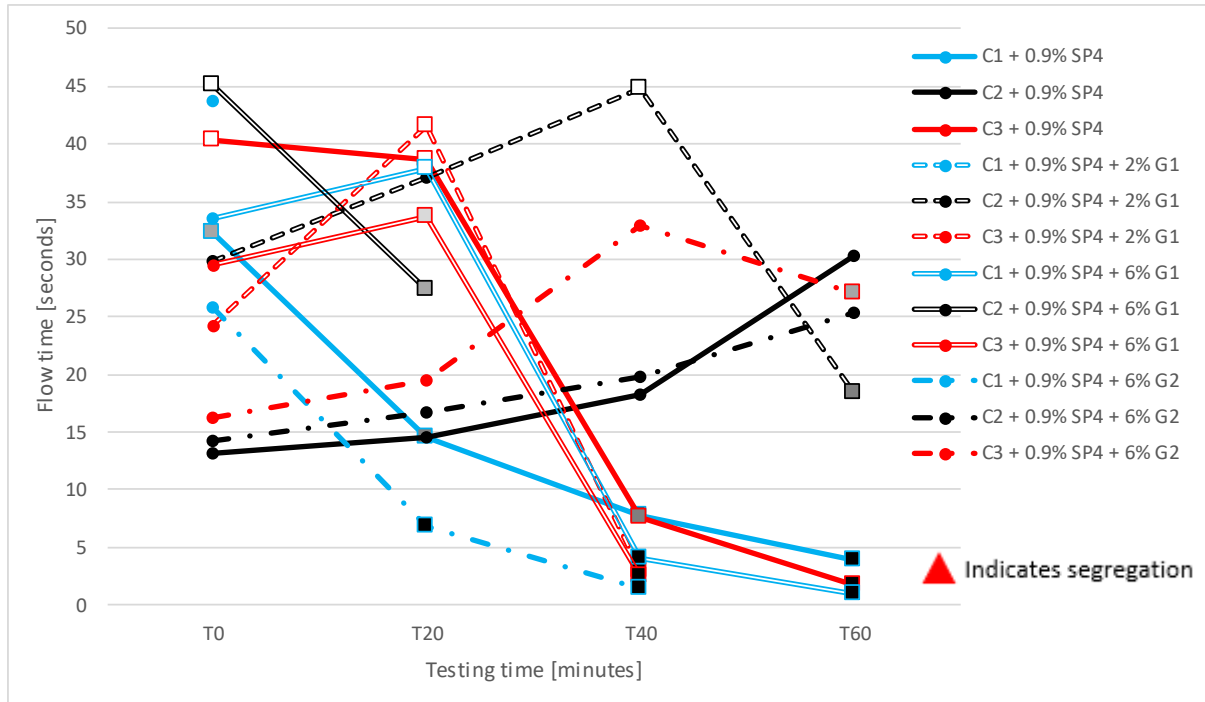


Figure 5.26: Marsh cone test result for different clinkers in combination with 0.9% SP4 and bassanite/gypsum

### 5.2.3. Setting time

Considering the results when adding bassanite to a mix containing 0.2% superplasticiser.

When adding 2% and 6% bassanite to the mix containing SP1 respectively, seen in Figure 5.27, the final setting times stayed similar but that the initial set occurred much faster for the 6% addition.

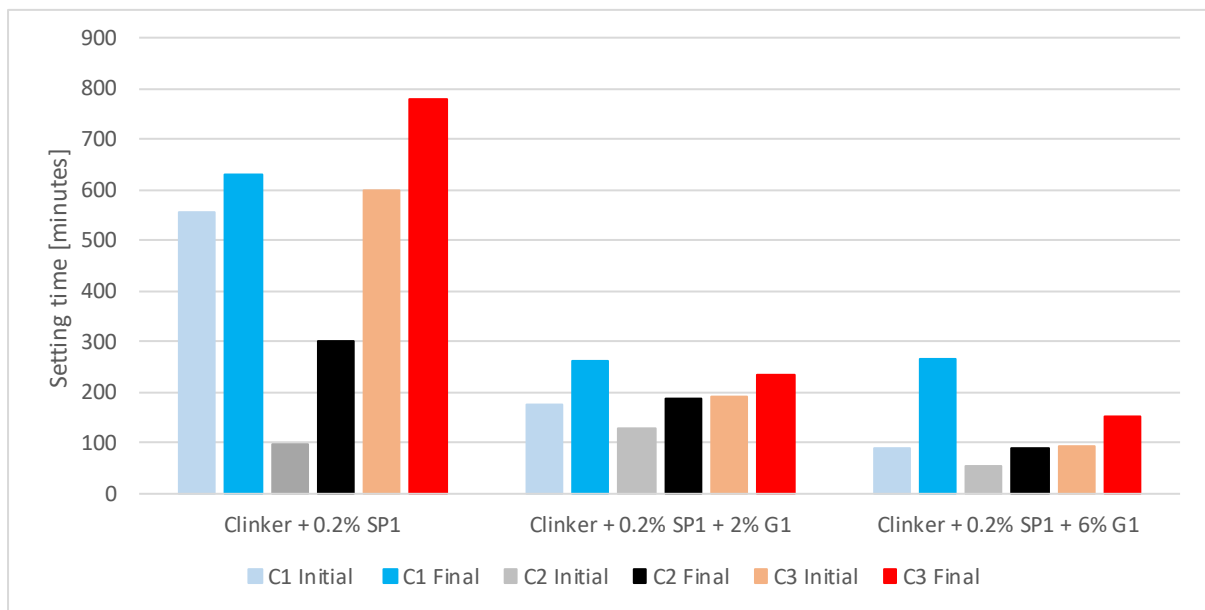


Figure 5.27: Setting time result for different clinkers in combination with 0.2% SP1 and bassanite

When considering SP2 as in Figure 5.28, the 2% and 6% bassanite additions reduced the setting times, with the 2% addition having a period between initial and final set of 23 minutes, while a much longer period of 69 minutes resulted for the 6% addition. For C1 it is shown that 0.2% dosage SP2 increased the setting times compared with SP1, while SP3 increased it even more than SP2.

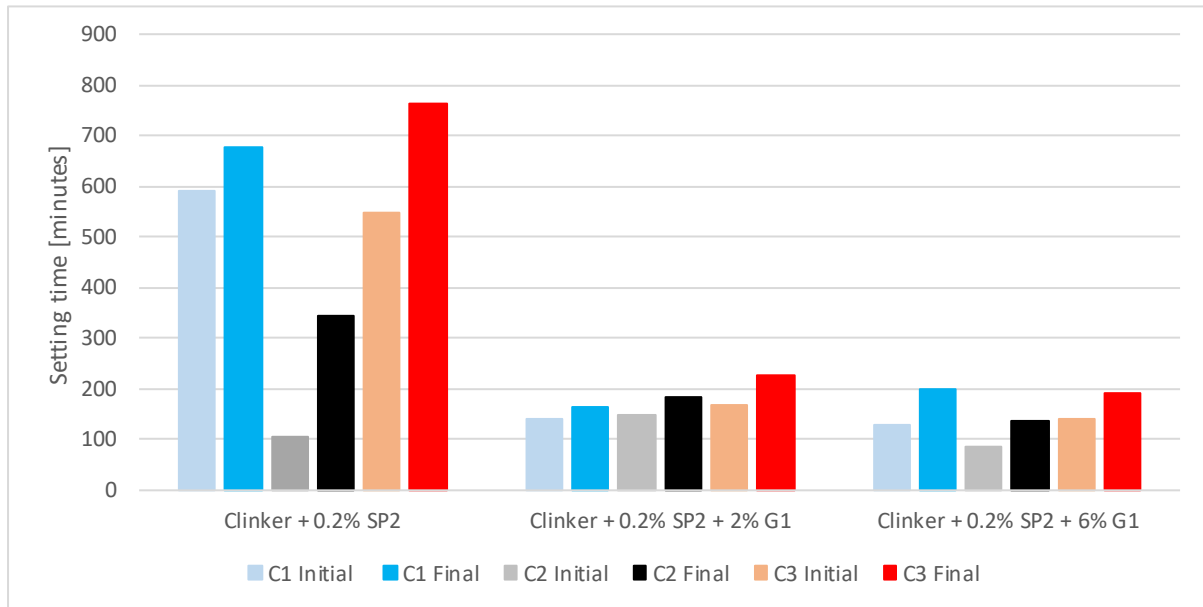


Figure 5.28: Setting time result for different clinkers in combination with 0.2% SP2 and bassanite

When adding 2% bassanite to the mixture containing SP3 as seen in Figure 5.29, a similar result to that of SP1 occurred, however, for the 6% bassanite addition, the initial set was quicker with the time required to reach final set, increasing creating a much longer period between the initial and final set.

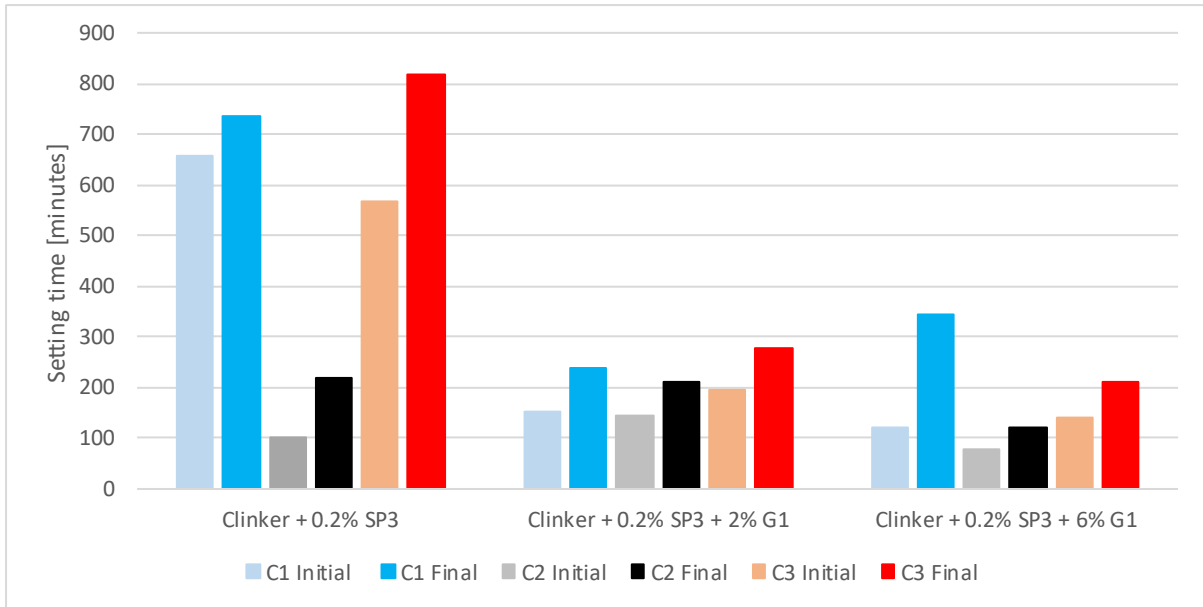


Figure 5.29: Setting time result for different clinkers in combination with 0.2% SP3 and bassanite

Figure 5.30 show, for SP4, both the initial and final setting times decreased as the addition of bassanite increased. The period between the initial and final set also increased as the addition increased.

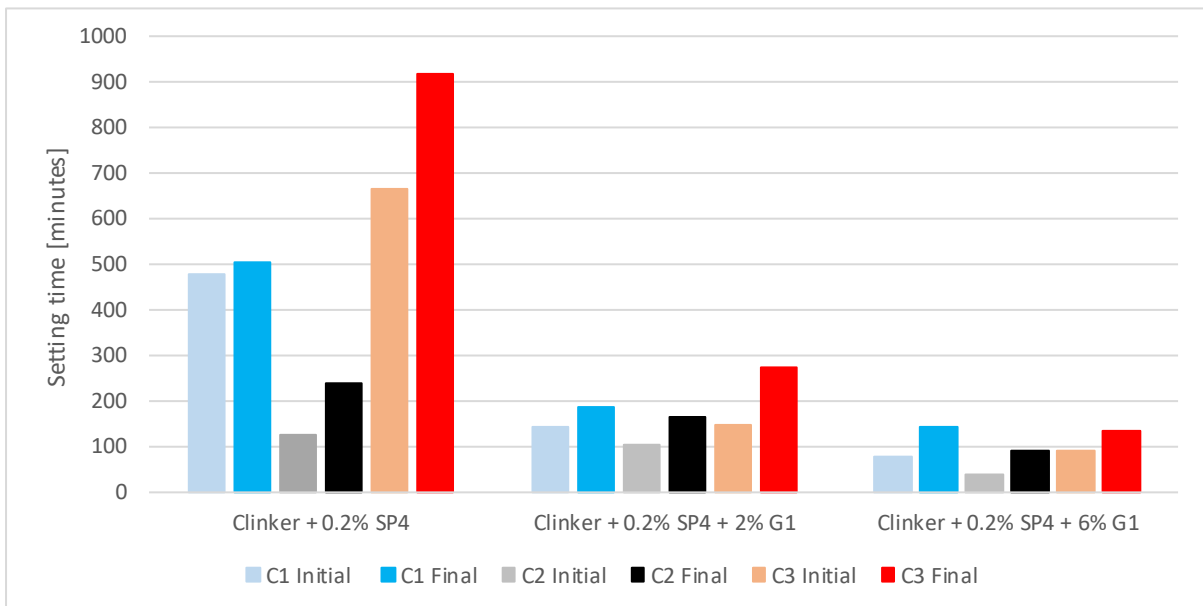


Figure 5.30: Setting time result for different clinkers in combination with 0.2% SP4 and bassanite

For C2 with the dosages of 0.2% SP1, SP2 and SP3 showed similar initial setting times while SP4 is found to increase this initial time. SP1 and SP2 resulted in higher final setting times compared to SP3



and SP4. Similar results are shown for SP2 with the initial setting time increasing with the addition of 2% bassanite and decreasing when adding 6% bassanite to the mix, while the final setting times are found to decrease as the percentage bassanite added increased. Again, similar results are shown for SP3, however, not much change is noted in the final setting time with the addition of 2% bassanite compared to that of the reference mix. SP4 also shows a decrease in the final setting time as the addition of bassanite added increased, however, unlike with the other superplasticisers, as the addition of bassanite increased, the initial setting time also decreased.

C3 showed similar periods between initial and final setting times for all the superplasticisers considered. SP1 and SP2 showed similar final setting times at 0.2% dosage while the initial setting time is found to be higher for SP1. Similar initial setting times is shown for SP2 and SP3, with SP3 having a higher final set than SP2. SP4 has the highest initial and final setting times. For the addition of 2% and 6% bassanite, for all the superplasticisers, both the initial and final setting times decreased proportionally as the percentage of the bassanite added increased. SP3 showed to have the longer period between initial and final set compared to SP1 and 2, with the addition of 2% bassanite to SP4 showing the longest period between initial and final set, with this period decreasing drastically for the 6% bassanite addition.

Figure 5.31 shows the results when adding bassanite and gypsum respectively to a mix containing 0.9% SP1. When considering SP1 in combination with the 6% bassanite addition the figure shows the biggest decrease in both initial and final set for C2 and C3, while the 2% bassanite resulted in the second biggest decrease in the setting times and the 6% gypsum causing the smallest decrease in setting times for these two clinkers. For C1 the 2% bassanite addition delayed the setting times the most. The 6% gypsum addition showed the smallest effect in the decrease of the initial setting time while the 6% bassanite showed the smallest effect on the final setting time of the mix.

Considering SP1, it is shown that the addition of bassanite decreased the final setting time, with the higher dosage causing the bigger delay in the final setting time. The 2% addition, in turn, increased the initial setting time with the 6% addition decreasing the time to initial set.

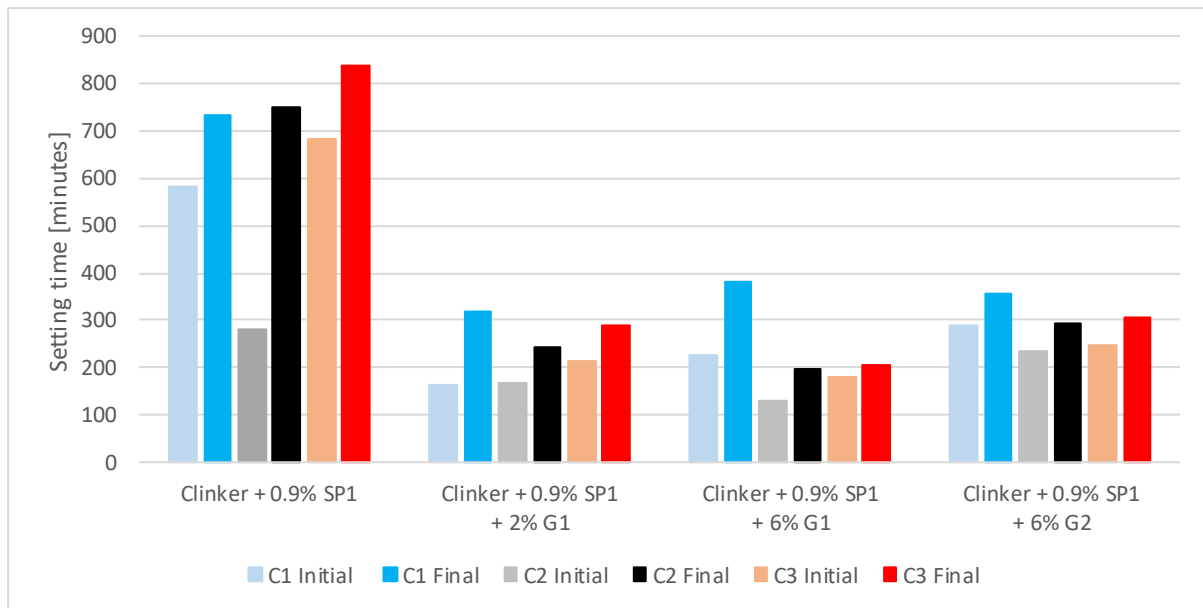


Figure 5.31: Setting time result for different clinkers in combination with 0.9% SP1 and bassanite/gypsum

Similar to SP1, when considering SP2 as seen in Figure 5.32, it is shown that the 6% bassanite addition resulted in the biggest decrease in both the initial and final set for both C2 and C3, with 2% bassanite having the biggest delay in the setting times of C1. Similar results were obtained for the decrease in setting times when considering the 2% bassanite and 6% gypsum additions when used in combination with C3. For C2, both the 2% bassanite and 6% gypsum additions both resulted in an increased initial set with the 6% gypsum addition slightly increasing the final setting time and the 2% bassanite addition causing a delay in the final set. Both the 6% bassanite and gypsum additions decreased the initial and final setting times of C1, with the delay in set being significantly longer for the gypsum addition than for the bassanite.

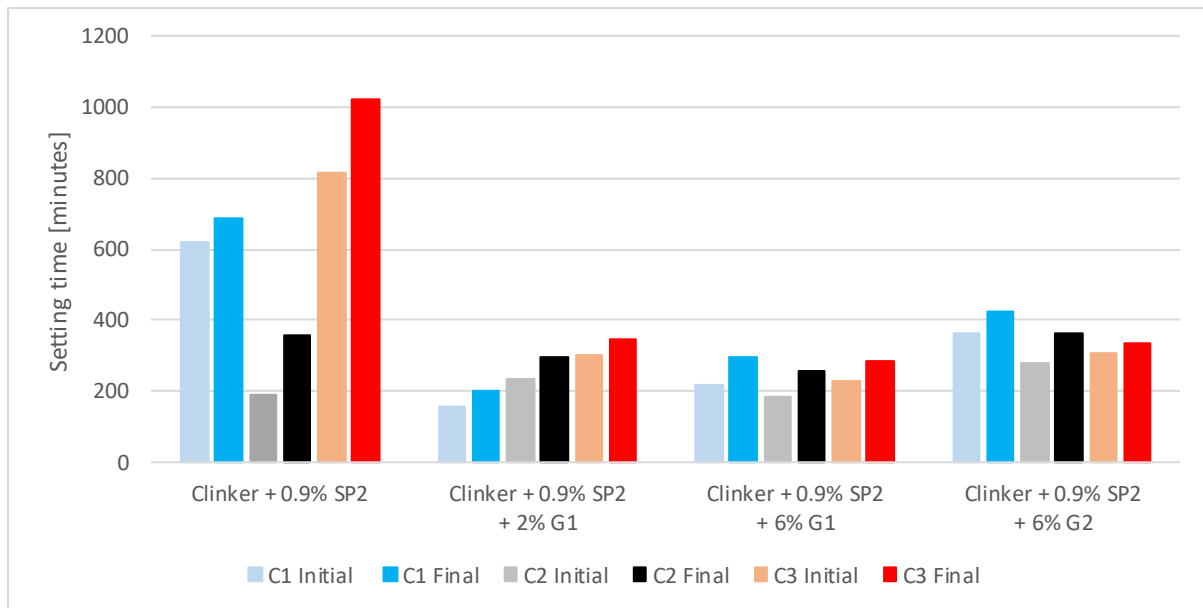


Figure 5.32: Setting time result for different clinkers in combination with 0.9% SP2 and bassanite/gypsum

For SP3 in combination with C1, it is shown in Figure 5.33 that all of the additions decreased the setting times. The 2% bassanite resulted in the largest decrease in setting time followed by the 6% bassanite addition and then the 6% gypsum addition, which showed the smallest delay in setting time. For both C2 and C3, the 6% bassanite showed the lowest setting times of all the additions considered. Adding 6% bassanite resulted in the smallest increase in setting times for C2 and the largest decrease in setting times for C3. The 2% bassanite and the 6% gypsum additions increased the setting times of C2 respectively with the gypsum addition found to be most effective. Similar results for the decrease in initial setting times for C3 with 2% bassanite and 6% gypsum is shown, with only a minute difference between the two results, while the final setting time of the 2% bassanite addition showed a bigger delay than the 6% gypsum addition.

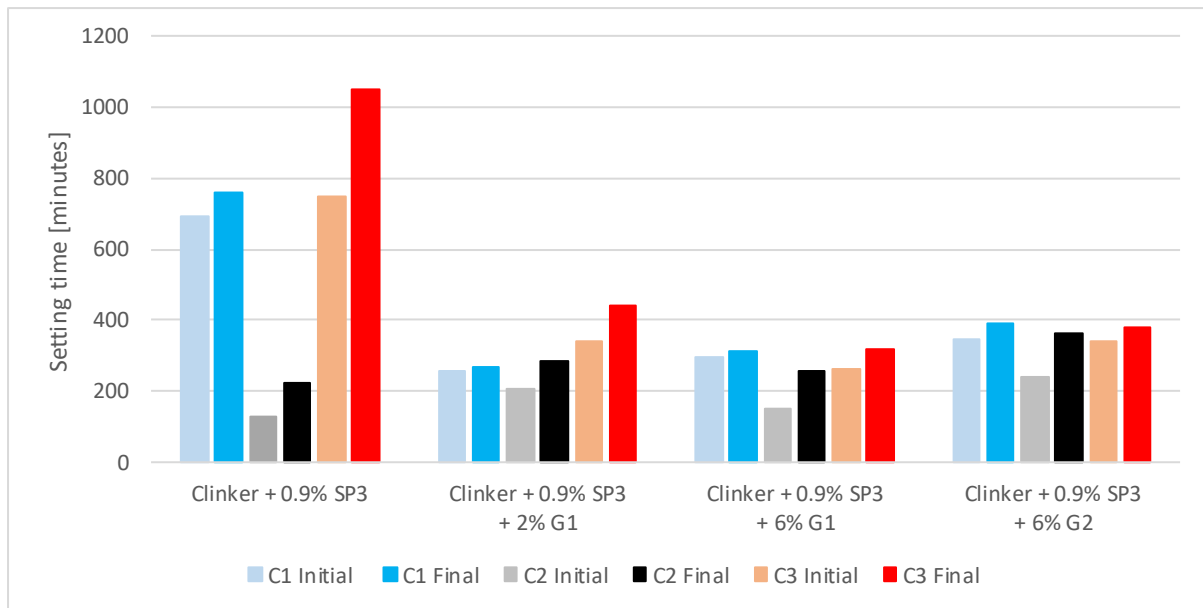


Figure 5.33: Setting time result for different clinkers in combination with 0.9% SP3 and bassanite/gypsum

Considering SP4 in Figure 5.34, a decrease in setting times occurred for all the mixes considered. The biggest percentage decrease in both the initial and final set is found for C1 with high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  contents. Similar initial setting times is found for C1 with the addition of 2% bassanite and 6% bassanite however, a slightly higher final set occurred for the 6% bassanite addition. The final setting time of the 6% gypsum addition is more than twice that of the bassanite addition while a significantly smaller difference in initial setting time is observed. This possible suggest that bassanite has a bigger impact on the setting time than gypsum with the reactivity thereof possibly being lower, as seen with the 2% and 6% bassanite addition. For C2, the 6% bassanite allowed for the biggest decrease in both initial and final setting times, with the 2% bassanite addition also reducing both settings times of the mix. While the 6% gypsum addition is found to also reduce the final setting time, to a lesser extent than the other additions, it is shown that the gypsum addition increased the initial set of the mix. For this specific clinker, C2, bassanite governs the decrease in setting times, similar to C1. C3, however, proved to react differently. While the 6% bassanite again resulted in the biggest decrease of both initial and final setting times, the 6% gypsum resulted in the second biggest decrease unlike with C1 and C2 where the 2% bassanite addition governed the gypsum addition. Adding 2% bassanite delivered an initial setting time only slightly higher than that of the 6% gypsum addition but resulted in a much higher final setting time compared to that of the gypsum addition.

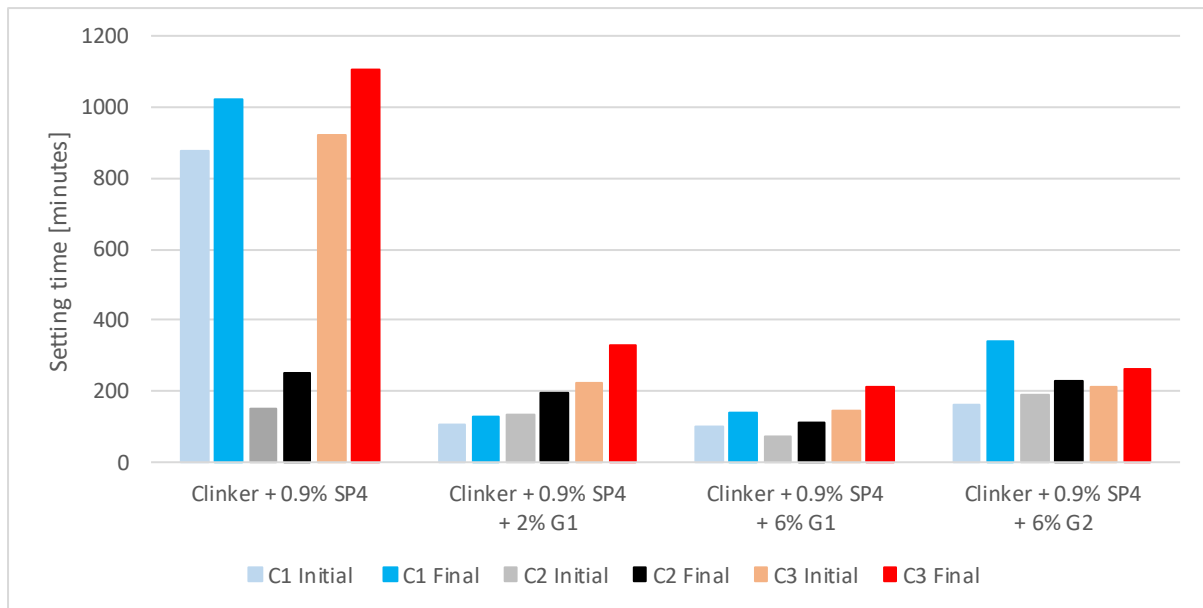


Figure 5.34: Setting time result for different clinkers in combination with 0.9% SP4 and bassanite/gypsum

#### 5.2.4. Compression strength

Figure 4.35 shows the results when adding bassanite to a mix containing 0.2% superplasticiser on the compressive strength of the mix.

Considering the addition of SP1 as seen in Figure 5.35, for C1, the addition of 2% bassanite did not cause much of a change in either the 2 or the 7-day strengths of the mix compared to that of the reference containing only superplasticiser, while the 6% bassanite increased both the 2 day as well as the 7-day strengths with about 8 MPa. It is interesting to find the increase in strength to be the same for both testing days considered, suggesting the increase in strength gain happens early in the hardening process of the paste. For C2, a decrease in both the 2 and 7-day compression strengths resulted in the addition of 2% bassanite, while the 6% bassanite addition caused an increase in the measured strengths. For C3, both the 2% and the 6% bassanite addition resulted in the same 2-day compressive strength, both higher than that of the reference mix. For the 7 day strengths, however, the 2% addition increased the strength slightly more than that of the 6% addition, both having a higher strength than the reference mix.

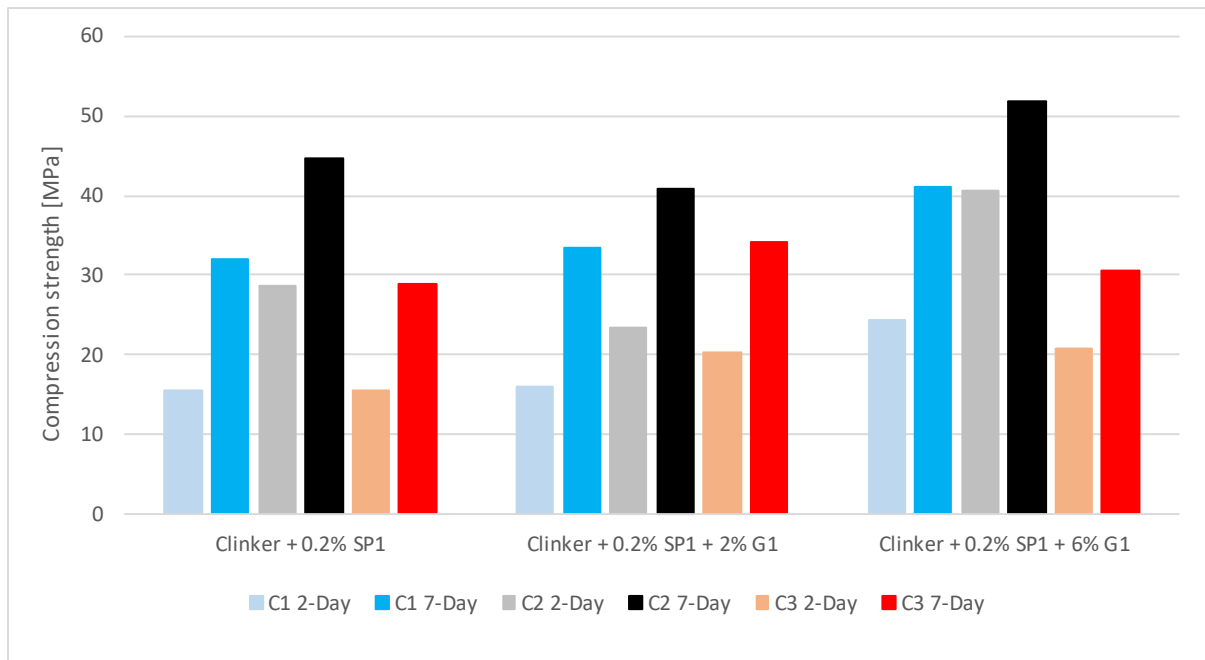


Figure 5.35: Strength test result for different clinkers in combination with 0.2% SP1 and bassanite

In Figure 5.36, SP2 when used in combination with C1, as with SP1, showed a bigger increase in both the 2 and 7-day compression strengths as the bassanite addition increases. For C2, when considering SP2, a slight decrease in strength occurred for the 2% bassanite addition while the strengths drastically increased when using the 6% bassanite addition. C3, again as with SP1, showed a similar increase in the 2-day strengths for both the 2% and 6% bassanite additions, while the 7-day strength associated with the 2% bassanite addition is 3 MPa higher than that of the mix containing 6% bassanite.

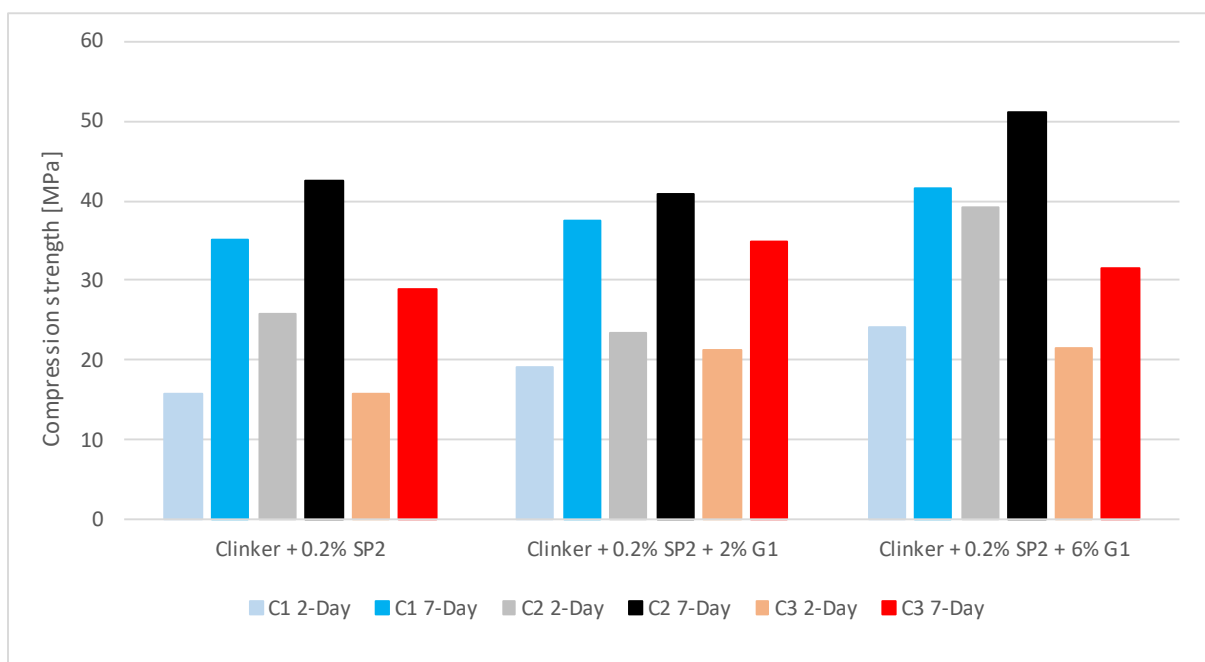


Figure 5.36: Strength test result for different clinkers in combination with 0.2% SP2 and bassanite

For SP3 again, seen in Figure 5.37, as with the previously mentioned superplasticisers, when used in combination with C1, resulted in an increased compression strength for both the 2 and 7-day tests with the mix gaining strength as the addition bassanite increases. C2 also caused a familiar result with the 2% addition of bassanite decreasing the compression strength measured at both the 2 day and 7 day testing times and the 6% addition causing an increase in strength. The strength gain for the 7-day result is however less significant than the results obtained for SP 1 and SP2. Similar reference mix results were obtained when considering C3 than when it used in combination with SP2 as mentioned. Both the 2% and 6% bassanite addition resulted in the same strength gain for the 2-day compression strength tests, with these values being found to be similar as for the 2% bassanite addition in combination with SP2. Again, with the 7-day results, similar values are obtained when comparing to SP2, with the 2% bassanite addition resulting in a bigger strength gain than the 6% addition. Comparing these results with the results obtained for SP2, it is evident that all values are similar with the biggest difference being 0.7 MPa.

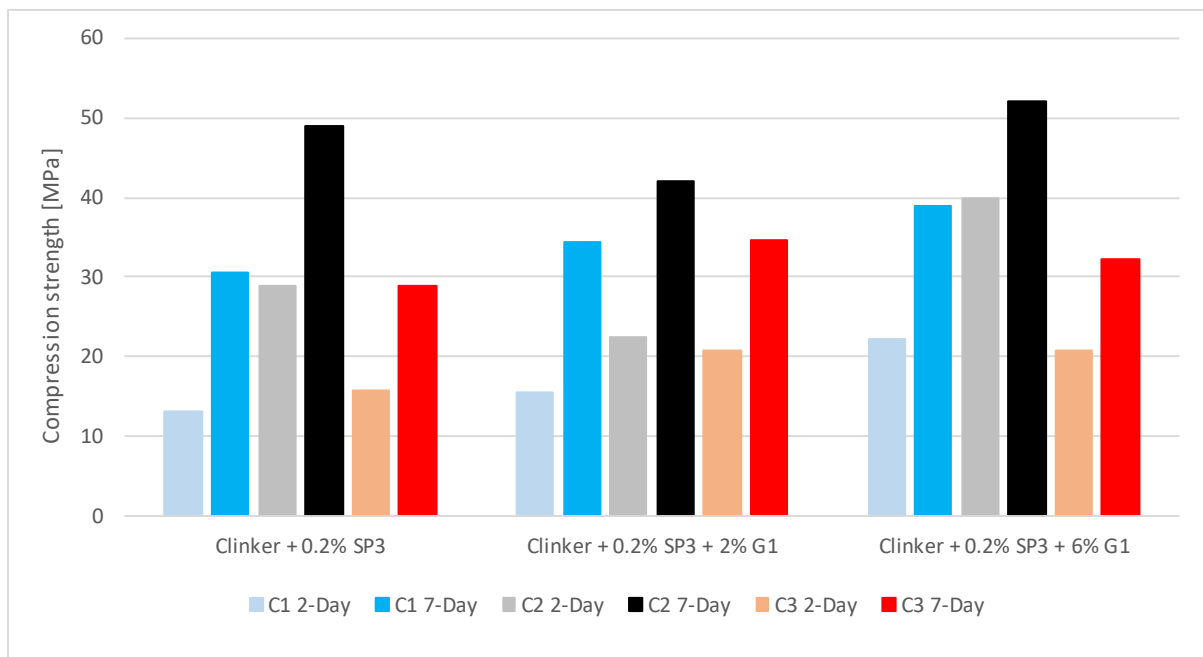


Figure 5.37: Strength test result for different clinkers in combination with 0.2% SP3 and bassanite

The effect of SP4 on the results can be seen in Figure 5.38 and show that similar to the other superplasticisers when used in combination with C1, the 2% bassanite addition showed a decrease in the compression strength of both the 2 and 7-day tests. However, SP4 resulted in a much larger decrease in strength for the 7-day result than the other superplasticisers considered. For the 6% addition, as expected, the 2-day compression strength increased again, while the 7-day strength is

slightly lower than that of the reference mix, unlike any other superplasticiser. Similar values are shown for the additions when using C2 as for the other superplasticisers with the 2% addition decreasing the strengths of the mixture and the 6% bassanite addition increasing the strengths. It is found that for the 7-day compression strength with the 6% bassanite addition, although an increase in strength is shown compared to that of the 2% addition, this is lower than that of the reference mix, which is not the case when using the other superplasticisers.

With the addition of both 2% and 6% bassanite, an increase in the 2-day compression strengths is shown respectively. However, a slight increase in strength is noted for the 2% addition compared to that of the 6% addition, unlike the results obtained for the other superplasticisers. As with the other superplasticisers considered, the 2% addition of bassanite increased the 7-day strength of the mix, while unlike with the other superplasticisers, the 6% addition of bassanite caused a slight decrease in the 7-day compression strength compared to that of the reference mix. For all clinker types considered, SP4 with the addition of 6% bassanite resulted in a decreased 7-day compression strength compared to that of the reference mix, where all other superplasticisers in this scenario resulted in a strength gain.

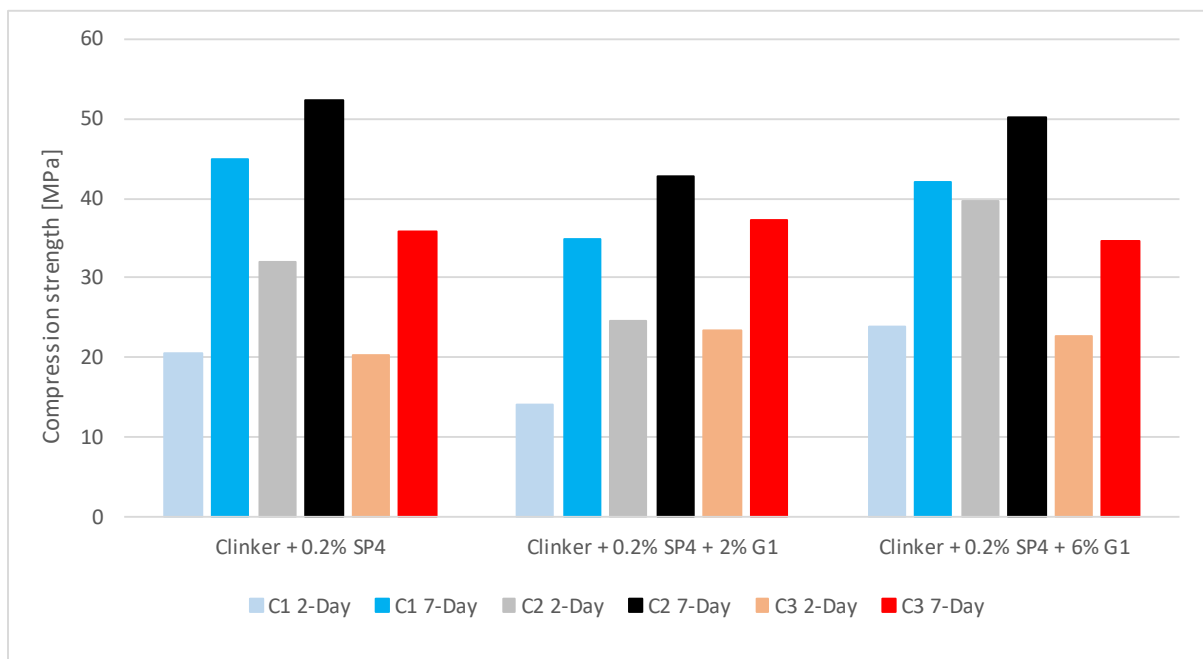


Figure 5.38: Strength test result for different clinkers in combination with 0.2% SP4 and bassanite

Figure 5.39 shows the effect the addition of bassanite has on the compressive strength of a mix containing 0.9% SP1. When using C1, the addition of 2% bassanite caused an increase in the



compression strengths for both the 2 day as well as the 7-day tests, with the 6% addition of bassanite increasing the strength of the mix even more. The 6% bassanite addition shows a more significant effect on the 2-day strength of the mixture. Adding 6% gypsum to the mixture also increased both the 2 and 7-day strengths, to a greater extent than the 6% bassanite addition.

For C2, the 2% bassanite decreased the compressive strengths, with the 7-day strength having a more significant decrease in strength due to this addition than the 2-day strength. The 6% bassanite and 6% gypsum additions both increased the compressive strengths of the mixes respectively, to reach a similar value with the gypsum addition resulting in a slightly higher strength gain.

C3 showed a slight increase in the 2-day strength with the addition of 2% bassanite, while for the addition of 6% bassanite and 6% gypsum, a similar increase is noted. The 7-day strength tests resulted in a similar value for all three additions, being higher than that of the reference mix.

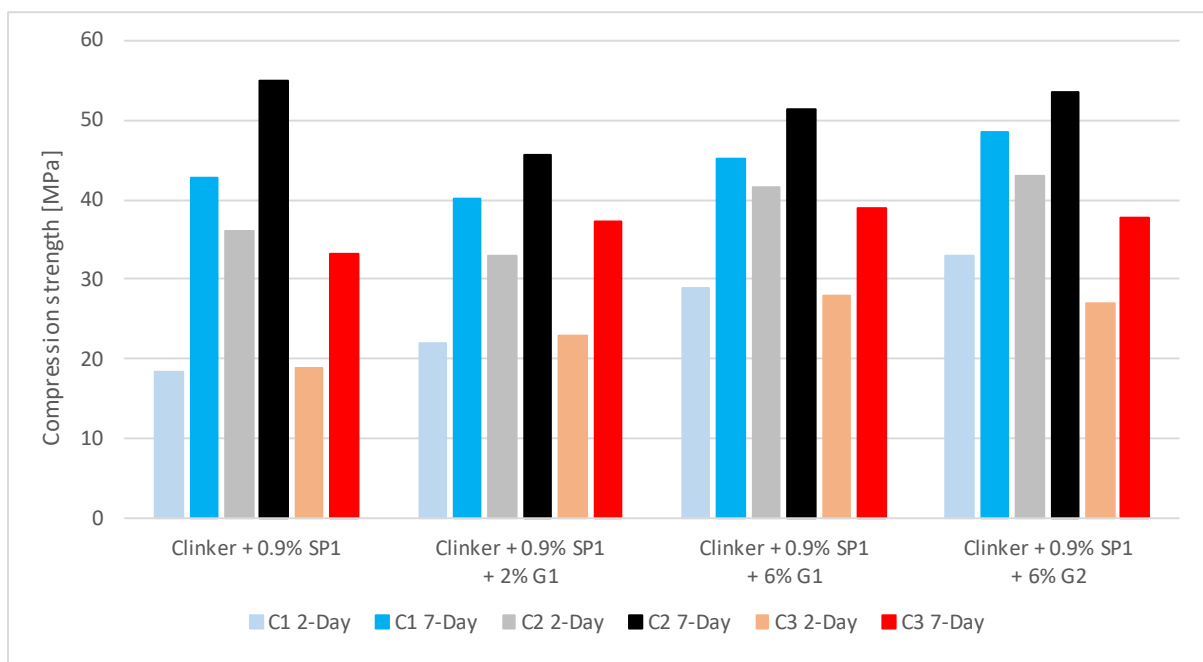


Figure 5.39: Strength test result for different clinkers in combination with 0.9% SP1 and bassanite/gypsum

SP2, as seen in Figure 5.40, together with C1 showed a 7 MPa increase in both the 2 and 7-day compressive strengths when considering the 2% bassanite addition, while an even bigger increase occurred for the 6% bassanite and 6% gypsum additions, which resulted in the same increased compression strength. C2 showed a decrease in compressive strength with the addition of 2% bassanite, with the decrease in strength being slight for the 2-day test but increasing when considering the 7-day test. This may suggest that the bassanite addition only affects the long-term strength gain

and not as much the initial strength gain at such low dosages. The 6% bassanite addition resulted in an increased 2-day strength compared to that of the 2% addition, while the 7-day strength also increased from the 2% addition, it is still found to be slightly lower than that of the reference mix. A slight increase in compression strength, of 3 MPa, was found compared to that of the 6% bassanite addition for the mix with the addition of 6% gypsum. The 7-day strength of the 6% gypsum addition is similar to that of the reference mix.

For C3, a similar compression strength was found for the reference mix containing only superplasticiser measured at both day 2 and day 7. With the addition of 2% bassanite, these strengths increased rather significantly, especially for the 7-day results. The additions of 6% bassanite and 6% gypsum respectively, resulted in a similar, slightly higher compressive strengths compared to that of the 2% addition when tested at 2-day strength, while similar results occurred to that of the 2% addition for both of the 6% additions at the 7-day testing period.

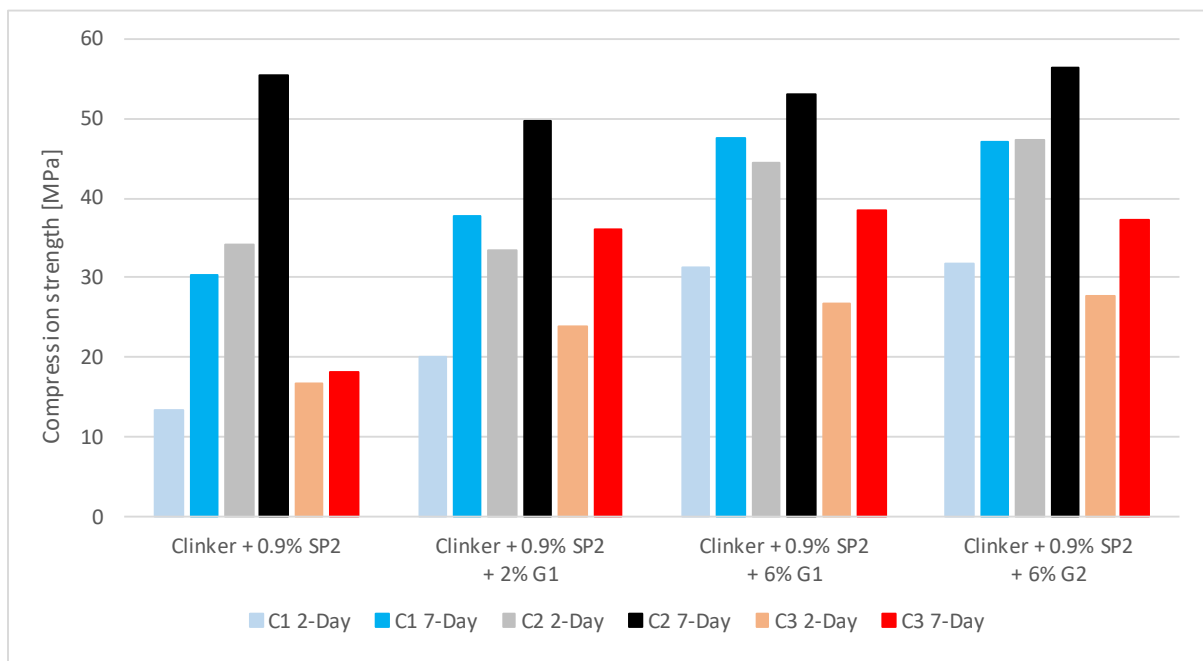


Figure 5.40: Strength test result for different clinkers in combination with 0.9% SP2 and bassanite/gypsum

Figure 5.41 shows the results when considering SP3. For C1, a significant increase in both the 2-day as well as the 7-day compressive strengths occurred for the mix containing a 2% bassanite addition, with both values increasing by a similar amount. Suggesting the addition aids in initial strength gain as opposed to late strength gain. With the 6% bassanite addition, a substantial increase, similar in size, is again found for both testing times compared to that of the 2% addition. When considering the 6%

gypsum addition compared to that of the 6% bassanite addition, the gypsum resulted in a slightly higher compressive strength than that of the bassanite, while the increase in strength is again similar for the different testing times.

C2 showed a decrease in both the compression strengths measured for the addition of 2% bassanite. The 7-day results of the mixes with 6% bassanite and 6% gypsum respectively, is the same as that of the reference mix. However, for the 2-day results, a similar increase in compression strength is noted for these two additions.

Considering C3, similar increases in the 7-day compression tests are shown for all three of the additions, with the 2% bassanite addition having the most significant increase in the 2-day strength. The 6% bassanite resulted in a slightly higher measured strength than the 2% addition, while in turn, the 6% gypsum addition showed a similar increase in strength compared to the 6% bassanite addition.

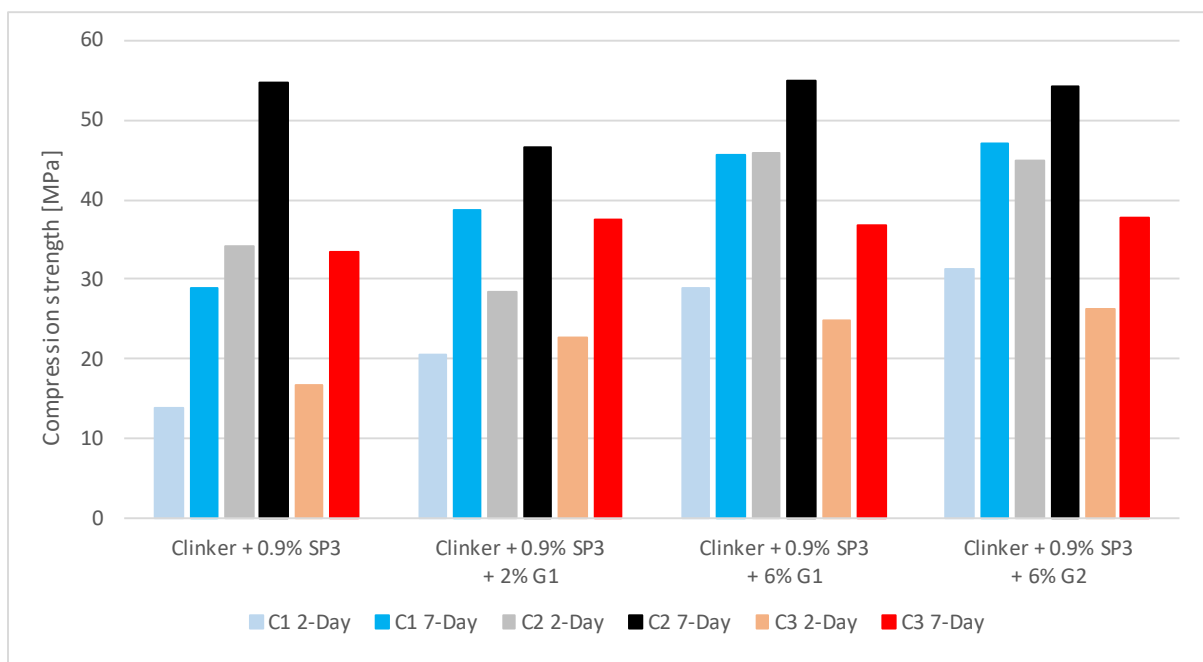


Figure 5.41: Strength test result for different clinkers in combination with 0.9% SP3 and bassanite/gypsum

C1, when using SP4 as seen in Figure 5.42, resulted in the same significant increase in the 7-day compression strength for all three the additions considered, while a similar increase occurred in the 2-day compression strengths for the 6% bassanite and 6% gypsum additions. While the 2% bassanite addition also resulted in an increased 2-day compression strength compared to that of the reference mix, it is slightly lower than that of the other two additions. It could be considered that these additions,

when used in this combination of clinker and superplasticiser, have a similar effect on the long-term strength gain while the size of the addition plays a role in the short-term strength gain.

Figure 5.42 shows that for C2, a decrease in both the 2-day and the 7-day compression strengths with the addition of 2% bassanite when compared to the reference mix. The addition of 6% bassanite and 6% gypsum respectively, increased the compressive strength of the mixes significantly compared to the reference mix, to find a similar strength at the 2-day testing time. These 6% additions also showed a similar strength when tested at the 7 days, increasing from the measured value for the 2% bassanite addition reaching a compressive strength similar to that of the reference mix.

Considering C3, the same increase in both the 2- and 7-day compression strengths occurred for the 6% bassanite and 6% gypsum additions, having the same strength at the 2-day testing and the 7-day testing. This result indicates no difference in the reaction when comparing bassanite and gypsum at this dosage for this unique set of variables. When considering the 2% bassanite addition, a slightly smaller increase in the 2-day compression strength is noted compared to the 6% additions, while a slightly larger increase in compression strength was found for the 2% bassanite at 7-day testing compared to that of the 6% additions. A higher dosage bassanite/gypsum could be considered to aid in short term strength gain while lower dosages help to increase the long-term strength gain.

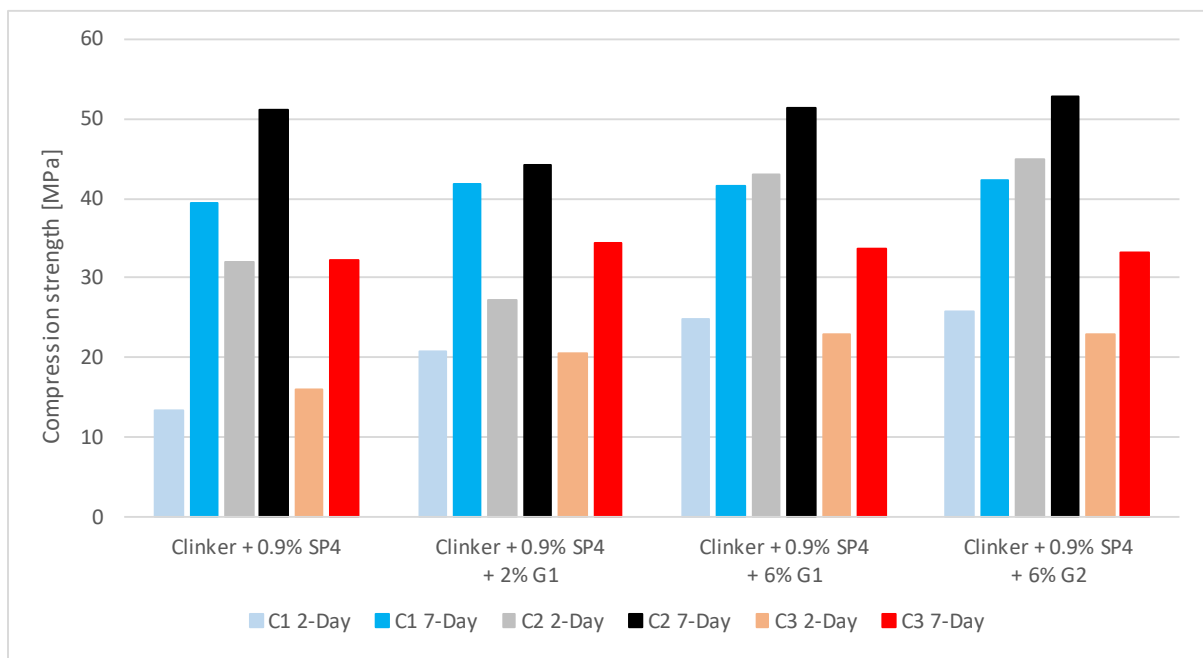


Figure 5.42: Strength test result for different clinkers in combination with 0.9% SP4 and bassanite/gypsum

### 5.2.5. Concluding summary

Considering the low dosage of 0.2% superplasticiser:

For SP1, all of the mixes was shown to decrease in flowability over time, while false set was found to occur for C1 with the 2% bassanite addition, after the initial testing time. SP2 again showed a decrease in slump flow over time for all the mixes, except for C2 with a 2% bassanite addition, which after testing time 20 minutes, showed a temporary increase in flowability. SP3, for C1 with 2% bassanite addition again caused false set after the initial testing time, while the initial flowability of the mixes containing C2 was found to decrease with the additions considered. SP4 was found to result in the lowest measured slump flows overall, with false set again occurring for C1 at the 2% bassanite addition. C3 with 2% bassanite addition was found to have the highest measured initial slump for SP4. For the Marsh cone tests considering the 0.2% superplasticiser dosage, a decrease in flowability was observed for all the mixes considered, with SP4 resulting in the most drastic loss in flowability.

Considering the high dosage of 0.9% superplasticiser:

The mini slump test showed for SP1, that the 6% bassanite addition resulted in the biggest increase in flowability, with the increased slump flow being maintained over time. For SP2, an increase in initial slump flow was found for all 2% bassanite additions, while C1 showed a drastic decrease in flowability after the 0 minute testing time and C2, without any bassanite additions was found to have the highest initial flowability. For SP3, it was found that for the 2% bassanite addition, the increased flowability decreased drastically for C1 after the initial testing. SP4 again resulted in false set for C1 with the addition of 2% bassanite. For the Marsh cone test, it was found that for SP1 segregation occurred at all testing times for the 6% bassanite addition, as well as the 2% addition when considering C2, with segregation taking place for C1 only at the initial testing time. For SP2, segregation occurred for all testing times when considering the 2% bassanite addition, while C1 resulted in the most drastic decrease in flowability. Overall similar results were obtained for SP2 and SP3, with the biggest difference being the decrease in flowability for the 6% addition mix of C2. SP4 showed the biggest decrease in flowability for all clinkers and all additions, with barely any flowability being observed as paste remained in the flow cone after initial testing for all additions considered.

The results of the mini slump- and Marsh cone tests in this section, confirms the conclusion of Yoshioka et al. (2002), stating that the adsorption of superplasticiser decreases significantly in the presence of calcium sulphate.

The superplasticiser was found to increase the setting times of the mixes, with the bassanite additions decreasing the setting times. C2 and C3 was found to show a bigger decrease in setting time as the addition bassanite increased, while for C3, at the 0.9% SP dosage, the initial setting times was found to decrease as the dosage increased for the 2% bassanite addition, while the setting times increased for the 6% addition compared to the 2% addition. At the 0.2% SP dosage, a bigger decrease was found in the setting times for the 2% bassanite addition then when adding 6% bassanite. Similar decreased results were however noted for both the initial and final setting times when considering SP4.

## 6. CONCLUSION AND RECOMMENDATIONS

This study aimed to use simple test methods to identify possible compatibility issues when using superplasticiser in a concrete mix, focussing on the interaction between the different mineral phases in clinker;  $C_2S$ ,  $C_3S$  and  $C_3A$ , calcium sulphate and superplasticiser, providing a starting point for further studies as to why these incompatibilities occur.

### 6.1. Summary of compatibility issues

A short discussion on the possible compatibility issues observed during this study. Any deviation from the reference result was considered as a potential secondary effect of the superplasticiser and in severe cases, as a compatibility issue between the clinker and the SP.

- With the addition of 2% bassanite and 0.9% of either SP2 or SP3, a significant decrease in flowability occurred for C1 when compared to C2 and C3, which both resulted in an increased flowability when considering these additions compared to that of the reference mix, indicating a possible incompatibility between the 2% bassanite addition and the high level  $C_4AF$  and medium  $C_2S$ ,  $C_3S$  and  $C_3A$  content, as well as the low total alkali associated with C1.
- When considering the 0.9% SP3 dosage together with the 6% bassanite addition, C2 resulted in a decreased flowability compared to that of the reference mix, with the flowability increasing gradually over time until a testing time of 40 minutes, where the flowability starts decreasing again. Unlike for C1 and C3, which resulted in an increased flowability, which remained constant over the testing period, compared to that of the reference mix. The high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content, as well as the high total alkali content of C2 in combination with the 6% bassanite addition, could suggest a compatibility issue when considering the high dosage SP3.
- For SP3, C1 resulted in a similar slump flow for all three dosages considered, with all three these results having a slump flow less than that of the reference mix. This indicates how this superplasticiser has a negative effect when used in combination with C1, which has a medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content, which could point to a possible incompatibility.
- For SP3, the results suggest that the 0.2% dosage loses its effectiveness in the first 20 minutes after initial testing when used in combination with C2, with the highest  $C_3S$  content, and lowest  $C_2S$ ,  $C_3A$  and  $C_4AF$  content.
- C2 was found to be the only clinker when used in combination with SP4, to result in a clear Marsh cone results at testing time = 0 minutes. which suggests a positive reaction between

the high  $C_3S$  content, and low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content of C2 and the naphthalene base of SP4.

- False set occurred when combining 2% gypsum/bassanite and C1. This false set also occurred at all 0.2% superplasticiser dosages when considering the 2% bassanite additions, while only 0.9% SP4 resulted in false set in combination with the 2% bassanite addition. The medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content of C1 thus react with the calcium sulphate to result in the formation of excessive ettringite. The 0.9% superplasticiser can however counter this reaction, while SP4 is unable to achieve this at the highest dosage considered in this study.
- Hardly any workability was noted for SP4 when considering the bassanite additions, while the 6% gypsum addition increased the flowability of the 0.9% dosage over time, for both C2 and C3. Suggesting an incompatibility between the bassanite and SP4, decreasing the effectiveness thereof, while in combination with C2 and C3, the gypsum addition increased the effectiveness of SP4.
- C3 was more prone to segregation when considering the high 0.9% dosage SP2 and SP3, in combination with the 2% bassanite and 6% gypsum additions, than the other clinkers which did not segregate. The 6% bassanite addition did not show any segregation for C3 at the mentioned superplasticiser dosages – only 6% gypsum. This indicates an incompatibility between the high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$  content of C3, with that of the addition of high dosages superplasticiser and the low addition bassanite and high dosage gypsum respectively. This could also suggest that C3 is more effective in the presence of high dosage calcium sulphate containing half water ( $CaSO_4 \cdot 0.5H_2O$ ) than of that containing two water ( $CaSO_4 \cdot 2H_2O$ ).
- 0.9% dosages of both SP2 and SP3 was found to increase the compression strength of C1 and C3 for all bassanite/gypsum additions considered. While for the 0.9% SP4 dosage, only the 2-day compression strength of C1 was found to be increased when considering the bassanite/gypsum additions. This suggests that the high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content of C2, react negatively with the calcium sulphate additions when used in combination with both SP2 and SP3, resulting in a loss of compressive strength. SP4 was found to decrease the strength of mixes containing bassanite or gypsum, suggesting an incompatibility between the two additions, however for C1 - which has a medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content, the bassanite ( $CaSO_4 \cdot 0.5H_2O$ ), as well as the gypsum ( $CaSO_4 \cdot 2H_2O$ ), resulted in an increase in the 2-day strength only.
- Segregation occurred for all clinkers, and all additions bassanite/gypsum, when considering the high 0.9% dosage SP1, with barely any segregation occurring (only at time 0 minutes for



C2) for the reference mixes. Suggesting that SP1 is less compatible with these additions than the other superplasticisers considered.

- Considering the 0.9% SP dosages, C1 decreased in setting times with the addition of bassanite, with the larger decrease associated with the smaller bassanite addition. For the 0.2% dosage, however, the smaller decrease occurred for the smaller bassanite addition, while for the 6% addition, the initial setting time decreased compared to that of the 2% addition, while the final setting time increased compared to the 2% addition.
- The dosage of 0.9% SP4 has the biggest impact on the setting times considering only superplasticisers on C1. SP1 showed to have barely any influence on the setting times of C2, with SP2, SP3 and SP4 showing an increased setting time, with similar results being observed for C3. The high dosages SP2, SP3 and SP4 showed to have drastic increases on the setting time of C3.
- The addition of 2% gypsum/bassanite respectively, decreased both the 2- and 7-day strengths of the mixes containing C1 and C2, while the strength of the C3 mixes, increased with these additions. The 6% gypsum, as well as the 6% bassanite additions, increased the 2-day strengths for all three clinkers, while the 7-day strengths were similar to that of the reference mixes.
- The SP1 dosages lowered the overall strength of the mixes, while that of the 0.9% dosage for C1 and C3 as well as the 0.5% dosage for C2 resulted in strengths similar to the reference. An increase in strength resulted for C2 at the 0.9% dosage.
- SP2 showed an increase in strength for C2 at the 0.9% dosage, with the biggest decrease in strength for C1 found at the 0.5% dosage. C3 showed a decrease in strength as the dosage SP increased.
- A similar decrease in strength occurred for all dosages of SP3 when considering C1 and C2. C3 also showed a slight decrease for the 0.2% dosage while similar results to that of the reference occurred for the 0.5% dosage, with a slight increase in strength for the 0.9% dosage.
- SP4 showed a decrease in strength as the dosage increased for all clinkers, with C2 showing an increased strength at the 0.5% dosage, after which it decreases again. The 0.9% dosage for C2 resulted in a similar 2-day strength than that of the reference mix.
- When considering the effect of the 0.9% SP1 dosage on that of the 6% gypsum addition, it was found that the SP1 increased the flowability of the mix for up to 40 minutes for C2 before it decreased in flowability again, while for C1 and C3, the effectiveness of the superplasticiser decreased straight away, albeit only slightly during the first 20 minutes, indicating a possible incompatibility between the gypsum addition together with the high SP1 dosage and the

chemical composition of C1 (medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content) and C3 (high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$ ).

- For C2, with a high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content, as well as the highest total alkali content, the 6% bassanite addition is the only addition considered to lower the initial slump flow of the mix compared to that of the reference mix. Considering C2 in combination with 2% and 6% gypsum additions respectively, similar 0-minute slump flows were observed, measured to have the biggest increase in slump flow.
- For the 0.9% SP2 dosage, the 6% G2 addition immediately showed a loss in flowability after the initial testing time for C1 (medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content), indicating that the superplasticiser was decreasing in effectiveness from the start. C2 and C3 resulted in a steady increase in slump flow over time, as the superplasticiser improved in effectiveness, suggesting a positive reaction between the different components.
- For SP1, when used in combination with the 6% sulphate additions, resulted in final setting times similar to that of the reference mix containing only SP1, but that the initial set occurred much faster for the 6% addition mix than for that of the reference, suggesting the sulphate speeds up the setting time initially, while possibly getting depleted in the process whereafter normal setting continues.
- Considering the 0.2% SP2 dosage, the flowability for C2 (high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content) was found to be lower for the mixes containing bassanite at testing time 0 minute, while after 20 minutes, the slump flow increased significantly for the mixes containing bassanite, with the 2% bassanite addition showing to be more effective in aiding the increase in slump flow than that of the 6% addition.
- The 0.9% SP4 resulted in an increased 2-day compression strength for C1, indicating a positive reaction between the naphthalene-based superplasticiser and the medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content of C1.
- The setting times were found to decrease significantly for C1 and C3 when used in combination with the bassanite/gypsum additions, while the setting times of the C2 mixes remained fairly constant for the additions. For the 0.2% superplasticiser dosages, a drastic loss in setting times was observed for both C1 (medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content) when used in combination with 2% bassanite additions, while for the 0.9% superplasticiser dosages, the 6% bassanite addition together with C3 (high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$ ) resulted in the largest decrease in setting times.

- When considering the 0.5% dosage SP4, C1 with a medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content showed to be the least effective as the flow nearly immediately stopped at this dosage.
- For the 0.2% SP1 dosage in combination with the 6% bassanite addition, C1 and C2 resulted in an increased 7-day strength, while only C2 showed an increase in the 2-day compression strength.
- For 0.2% SP4, with the addition of 6% bassanite, C1 with a medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content was found to have a rapid loss in workability compared to that of the reference mix containing only superplasticiser, suggesting an incompatibility between the bassanite ( $CaSO_4 \cdot 0.5H_2O$ ) and C1, or the bassanite and SP4.
- The 0.9% SP4 dosage resulted in a rapid loss in workability for the 6% gypsum addition when used in combination with C1 (medium  $C_3S$ ,  $C_2S$  and  $C_3A$ , and high  $C_4AF$  content), while an increased workability was observed for C2 (high  $C_3S$ , and a low  $C_2S$ ,  $C_3A$  and  $C_4AF$  content) and C3 (high  $C_2S$  and  $C_3A$ , medium  $C_4AF$  and low  $C_3S$ ).

## 6.2. Conclusion

The objectives of this study are to determine the effect of calcium sulphate and different types of superplasticiser, both respectively as well as in combination with each other, on the flowability of a paste consisting of sand, water and clinker, with varying  $C_3S$ ,  $C_3A$ ,  $C_4AF$  and alkali contents, while trying to identify incompatibilities between the various elements considered.

In summary, the study shows that both the gypsum and bassanite additions decrease the flowability of the paste, as the dosage increase. On the other hand, PCE superplasticisers increase the flowability of the mixture, proportionally to the dosage of the superplasticiser, with a the Naphthalene based superplasticiser, being less effective than the PCE superplasticisers. As specified by the manufacturer, SP2 is more compatible with cements manufactured in the Western Cape, which in this study is Clinker 2. SP3 is specified to be compatible with low alkali cements, which is also confirmed by the results of this study.

Various effects on the strength gain, setting times and flowability occurred when considering the different combinations of additions to the reference mixes, with possible compatibility issues being the cause thereof. Table 6.1 indicates roughly how many of the incompatibilities were found to be associated with the various levels of clinker phases present in the concrete mix.

Table 6.1: Summary of compatibility issues associated with different clinker phases

	High	Medium	Low
C <sub>3</sub> S	x x x x x	x x x x x x x x	x x
C <sub>2</sub> S	x x	x x x x x x x x	x x x x x
C <sub>3</sub> A	x x	x x x x x x x x	x x x x x
C <sub>4</sub> AF	x x x x x x x x	x x	x x x x x

The use of C1 (medium C<sub>3</sub>S, C<sub>2</sub>S and C<sub>3</sub>A, and high C<sub>4</sub>AF content) resulted in more compatibility issues than that of the other two clinkers combined, with C2 (high C<sub>3</sub>S, and a low C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF content) being associated with slightly fewer incompatibilities. C3 (high C<sub>2</sub>S and C<sub>3</sub>A, medium C<sub>4</sub>AF and low C<sub>3</sub>S) did not play a significant role when considering incompatibilities between the clinker composition, calcium sulphate and superplasticiser additions when compared to that of C1 and C2.

This study, however, only aimed to identify these inconsistent behaviours and incompatibilities, with further research needed to confirm the chemical reason behind it.

The recommended dosages for the superplasticisers used in this study was not exceeded when considering the arbitrary dosages used during the testing procedure and is it unlikely that any of these effects are related to overdosing of superplasticiser, while the high water:binder ratio may have an influence thereon.

It was also determined that these simple test methods can successfully be used to identify incompatibilities in a concrete mix, providing an easy approach to the on-site determination of concrete compatibility.

### 6.3. Recommendations

The following recommendations for futures studies can be made:

Determining the chemical composition of the superplasticisers. The chemical composition of various superplasticisers, which was unknown to us during this study, plays an important role on the mechanism and the effectiveness of the superplasticiser and could give an insight on how the specific superplasticiser react with a certain material. The backbone and chain lengths of PCE based superplasticisers vary from one PCE to another and should also be investigated.

More complex testing methods should be used; such as a rheometer, viscometer and heat flow calorimetry, to verify the results obtained from this study, which only considers simple test methods.

Various other SCMs should be incorporated to narrow down on the exact reaction responsible for the incompatibilities. The calcium sulphate should also be used in combination with other SCM, as literature suggests, for example, that the addition of limestone can affect the reactivity of the calcium sulphate.

The reaction between superplasticisers, calcium sulphate and the mineral phases of clinker can further be investigated by following the progression of the reaction through a microscope, or similar to SEM images, to verify results obtained from these studies.

The effect the various combinations of materials considered in this study have on the 28-day compression strength should be investigated, as well as other test methods to determine the effect of these additions on the long term properties of concrete, as this study only aimed to identify compatibility issues in the fresh concrete state.

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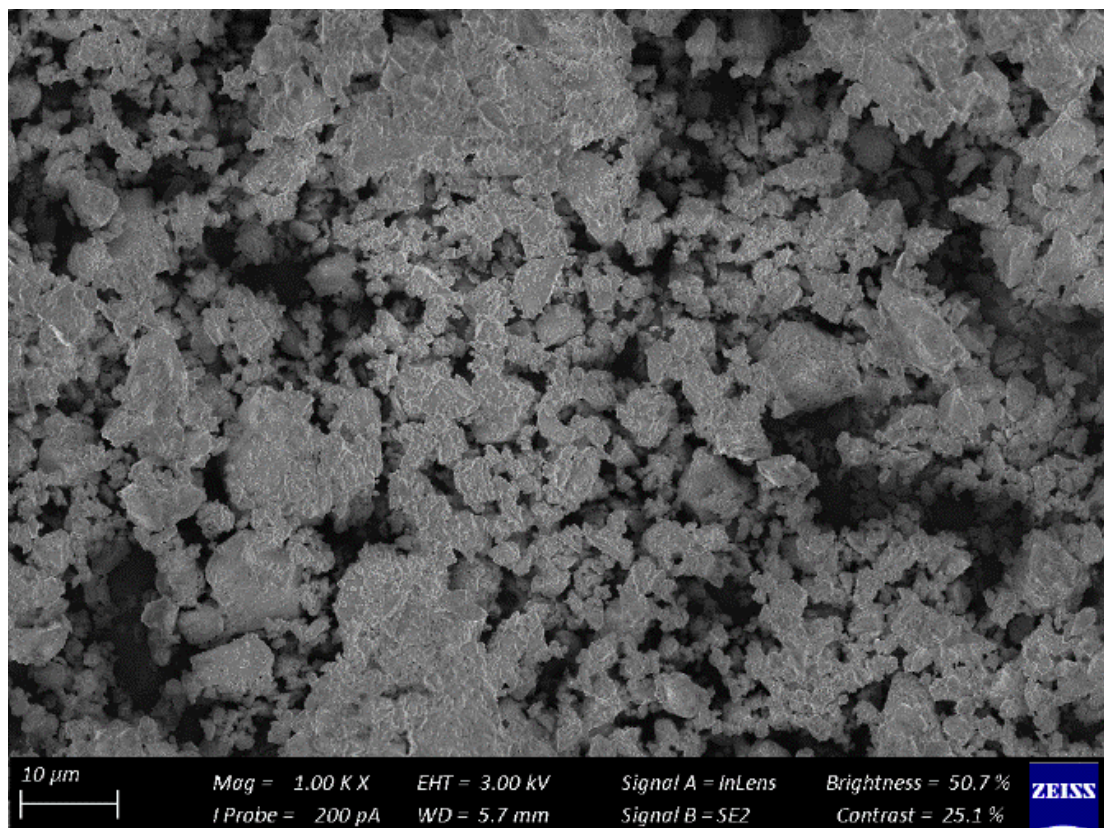
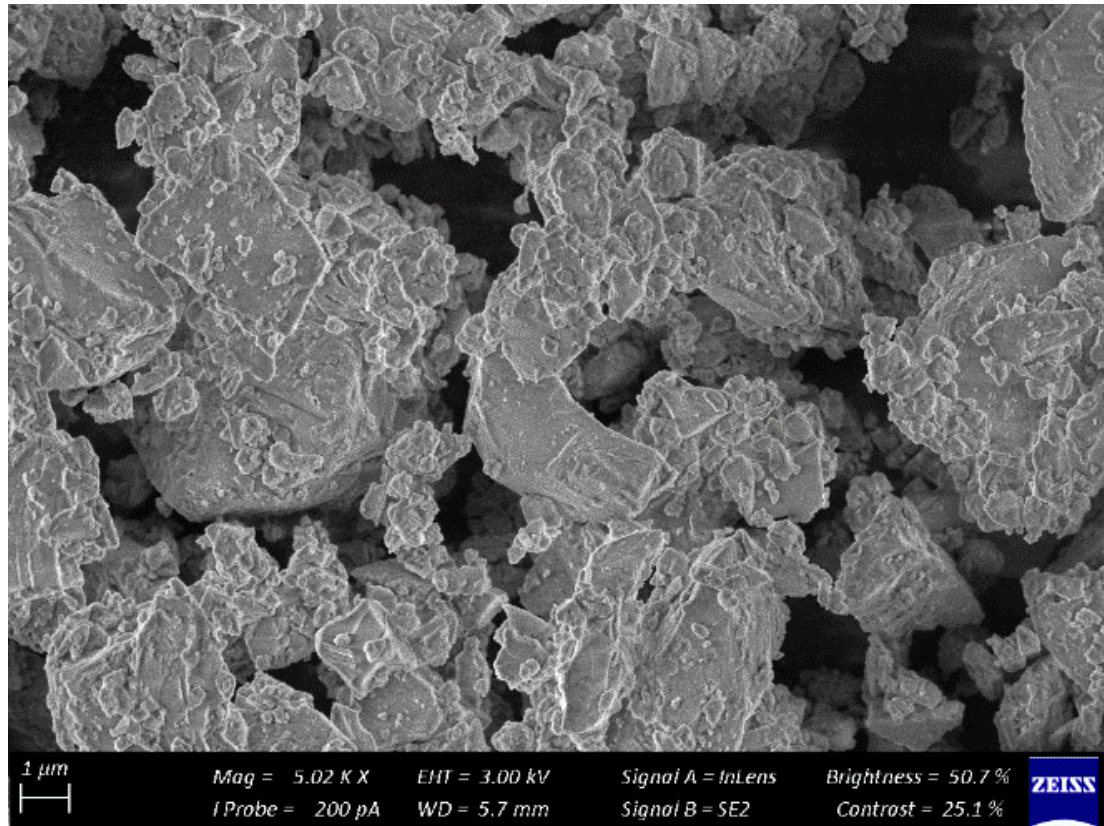
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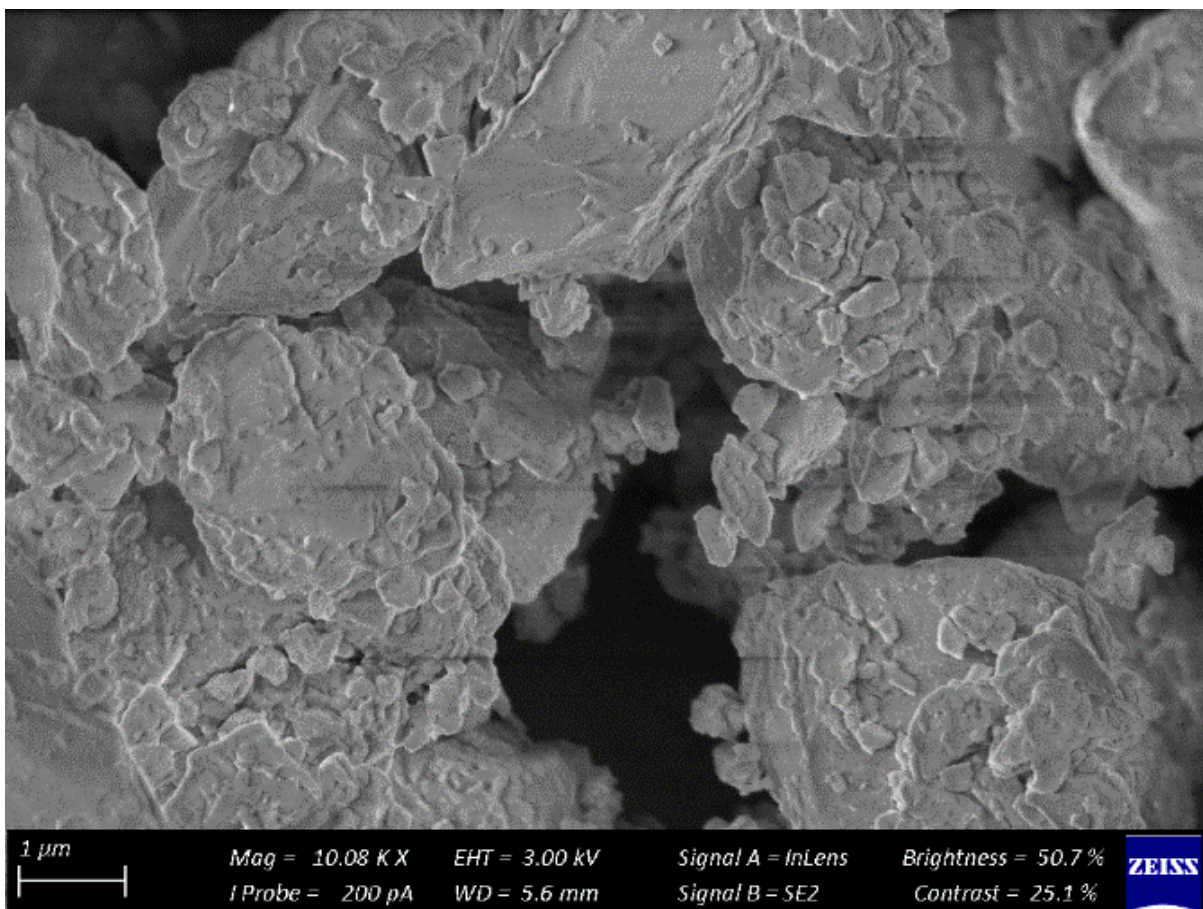
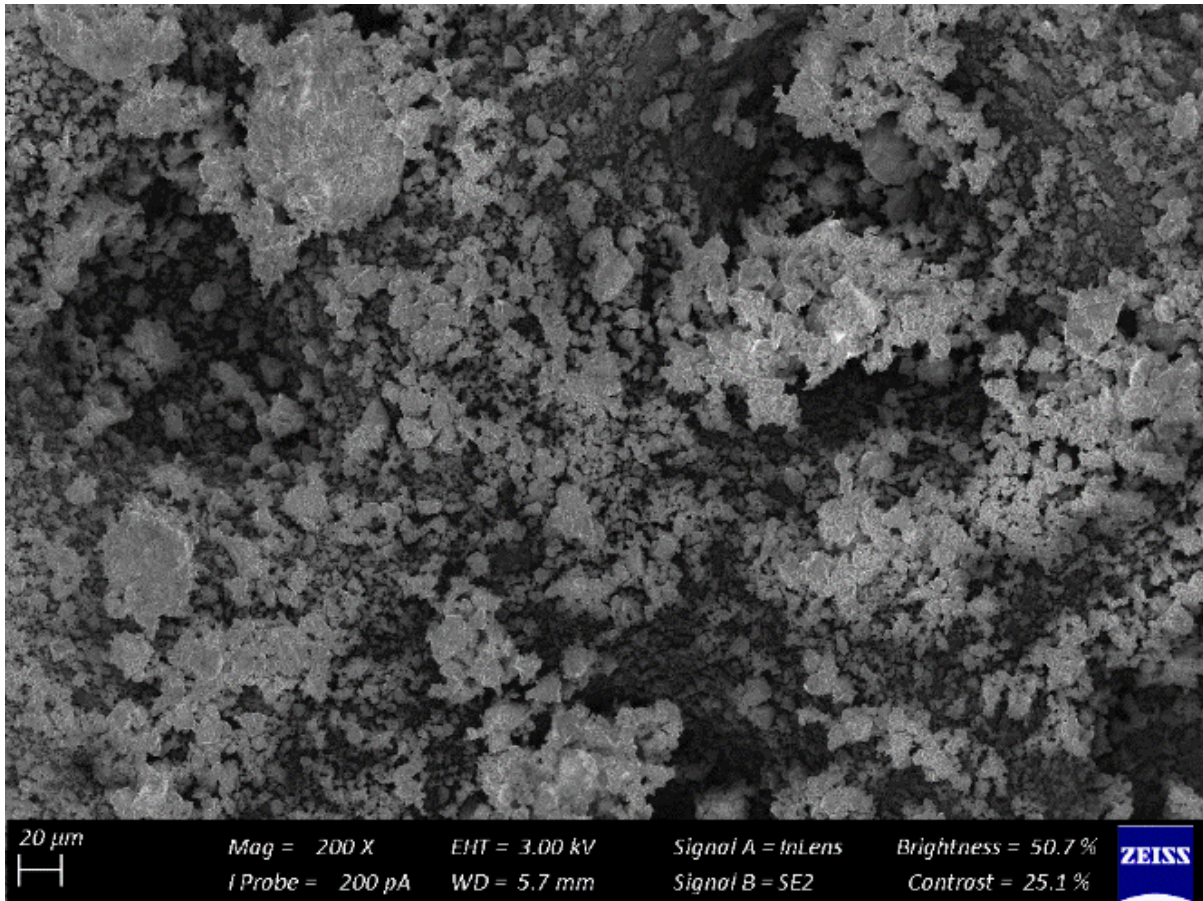
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## 8. Appendix A

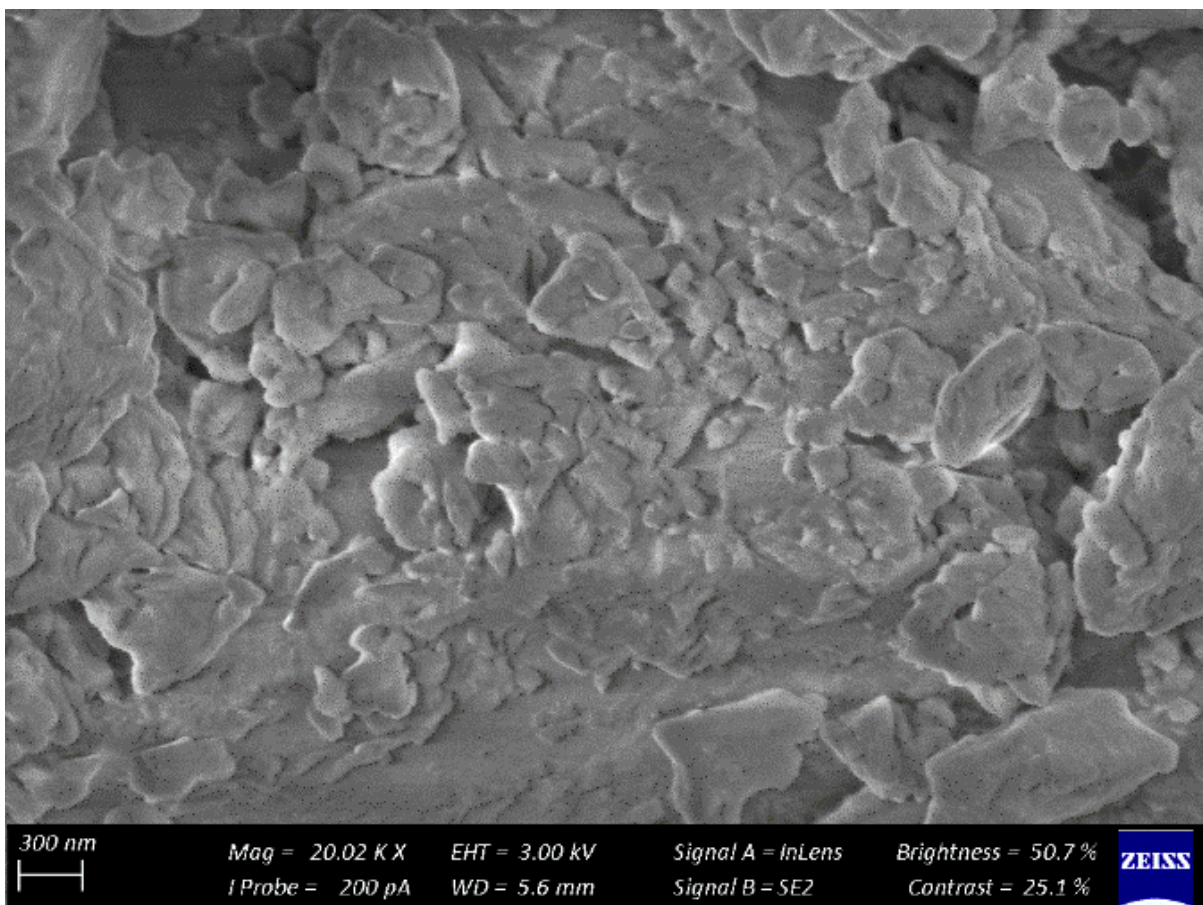
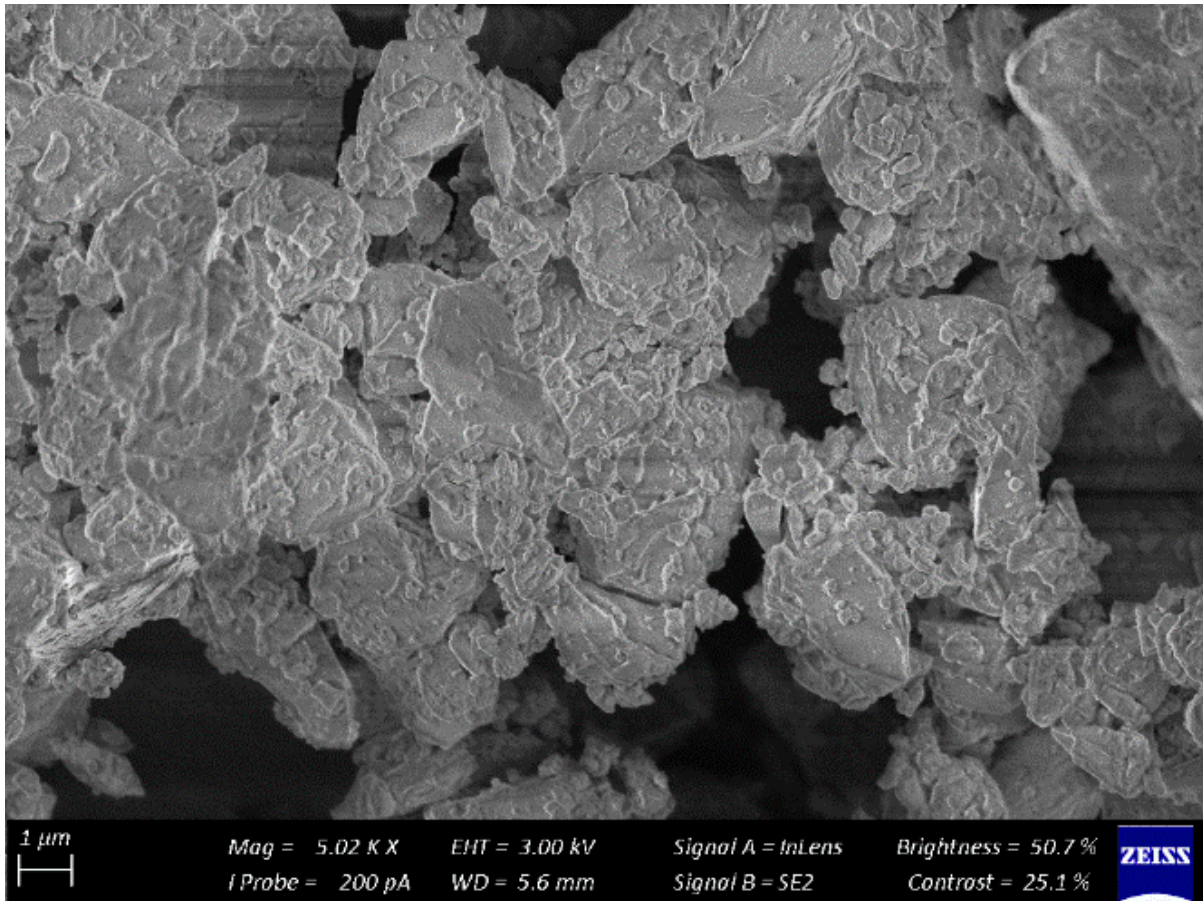
### 8.1. SEM images for C1 (Dwaalboom)



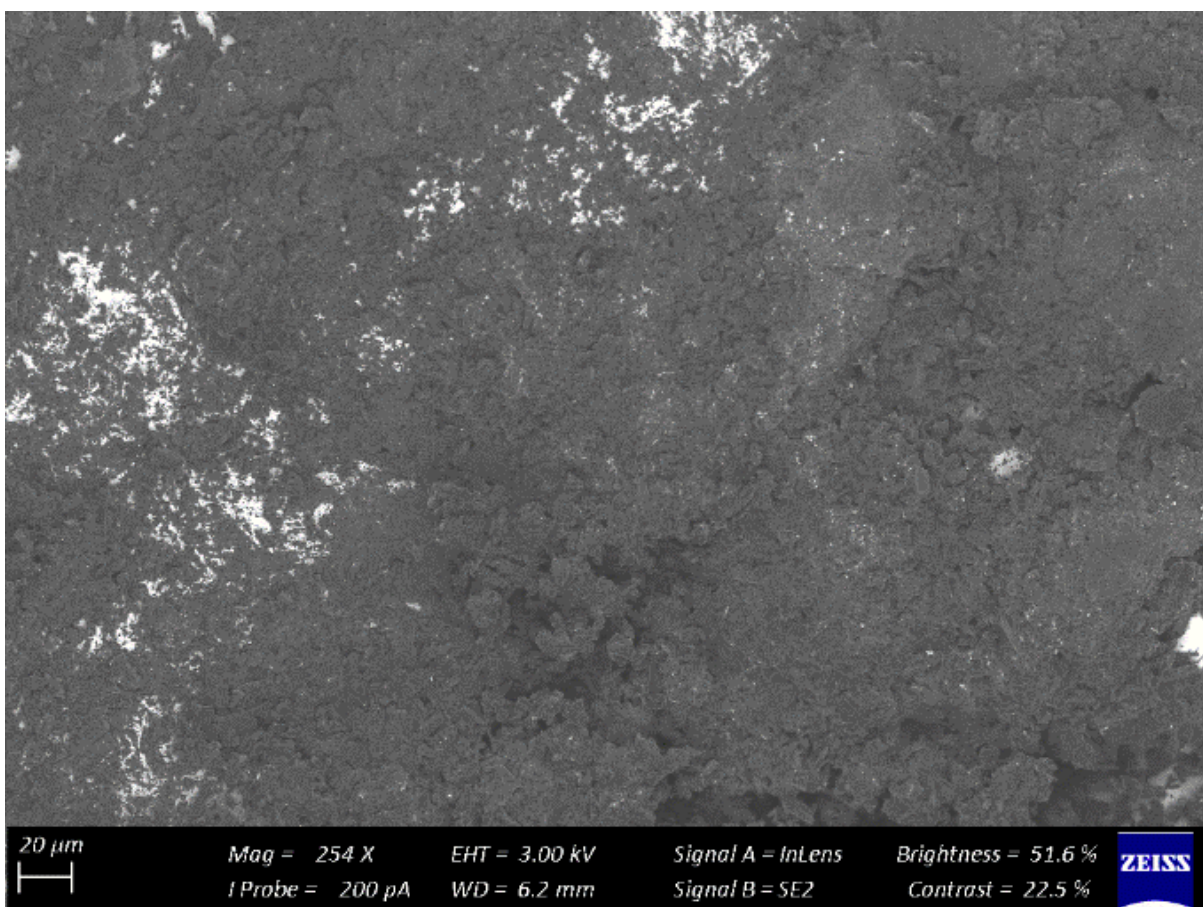
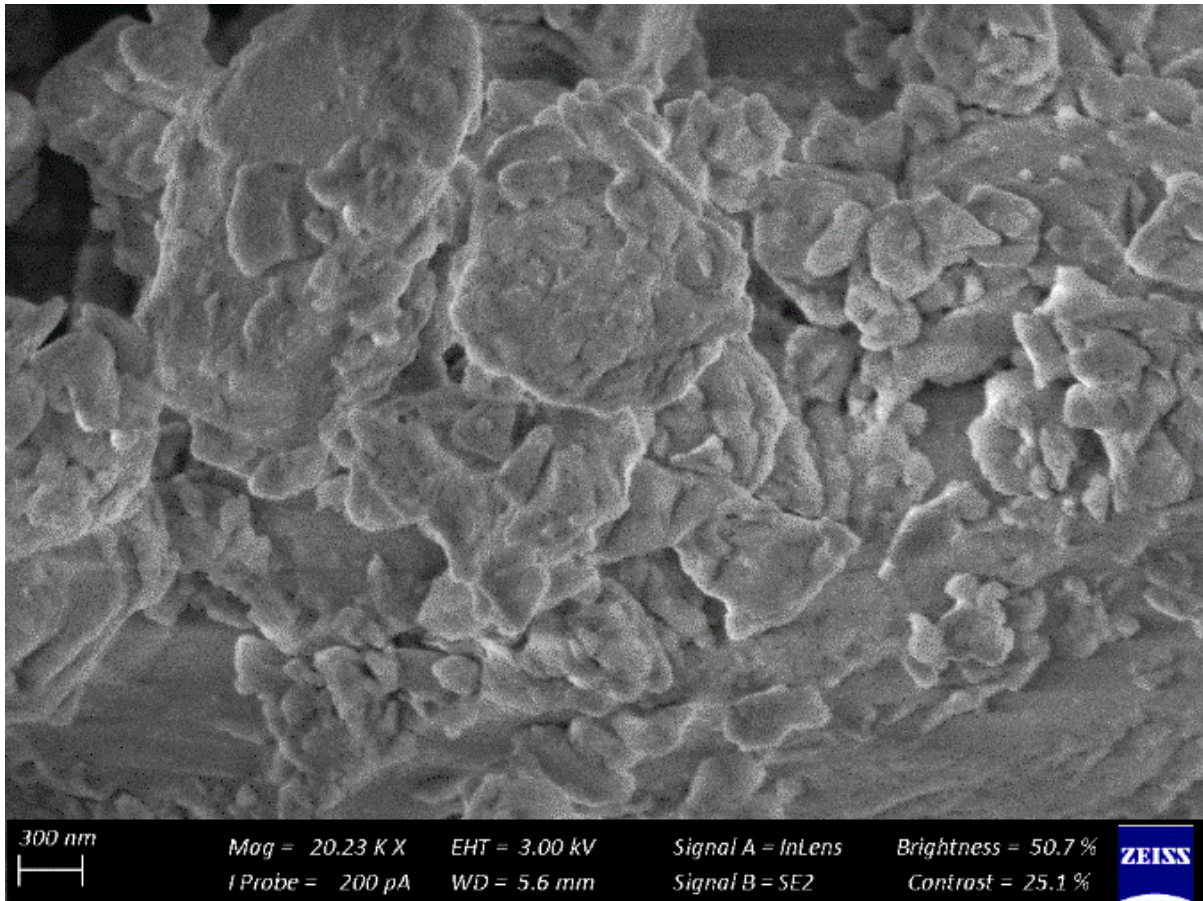






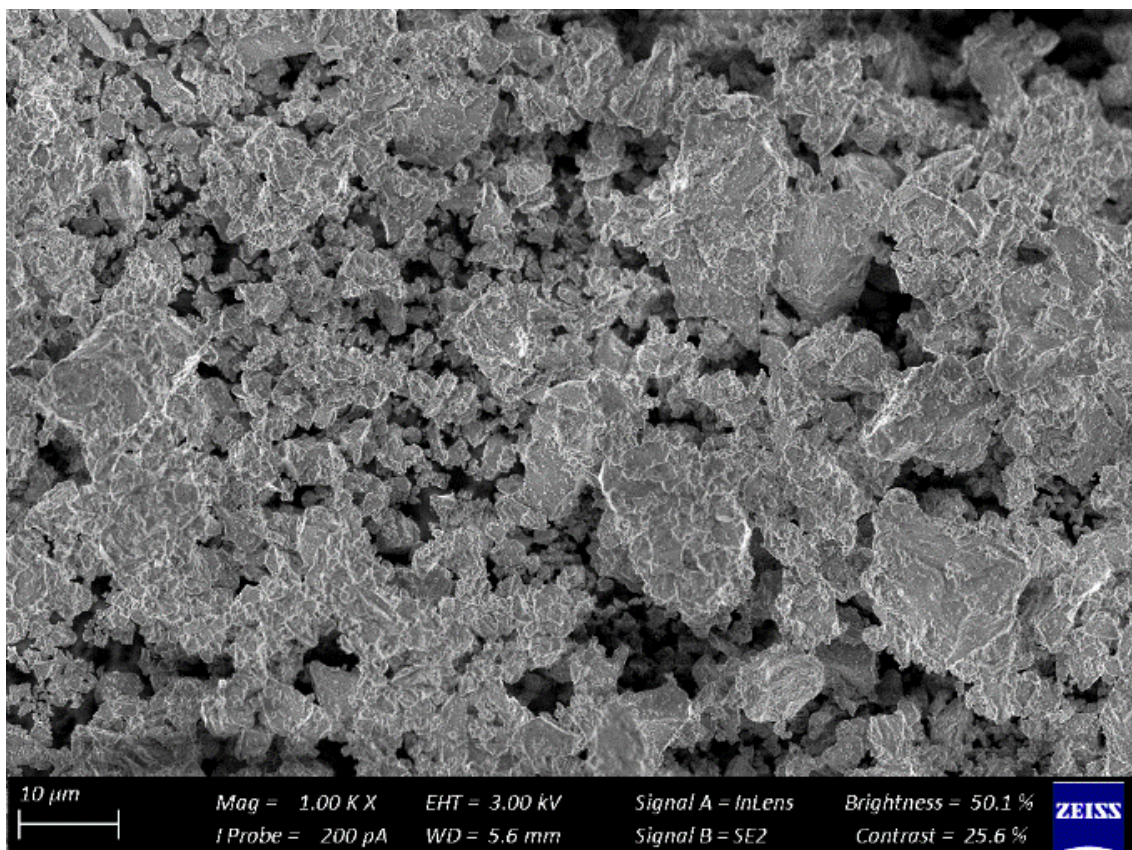
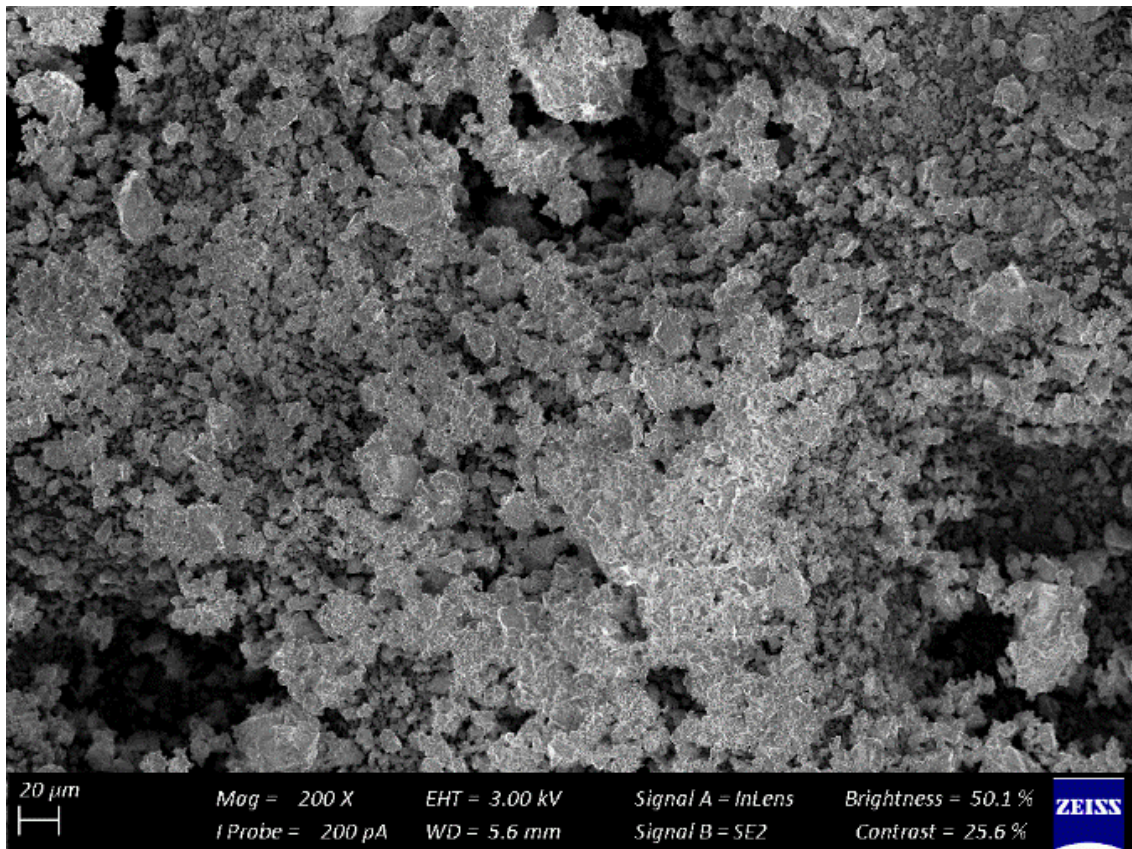




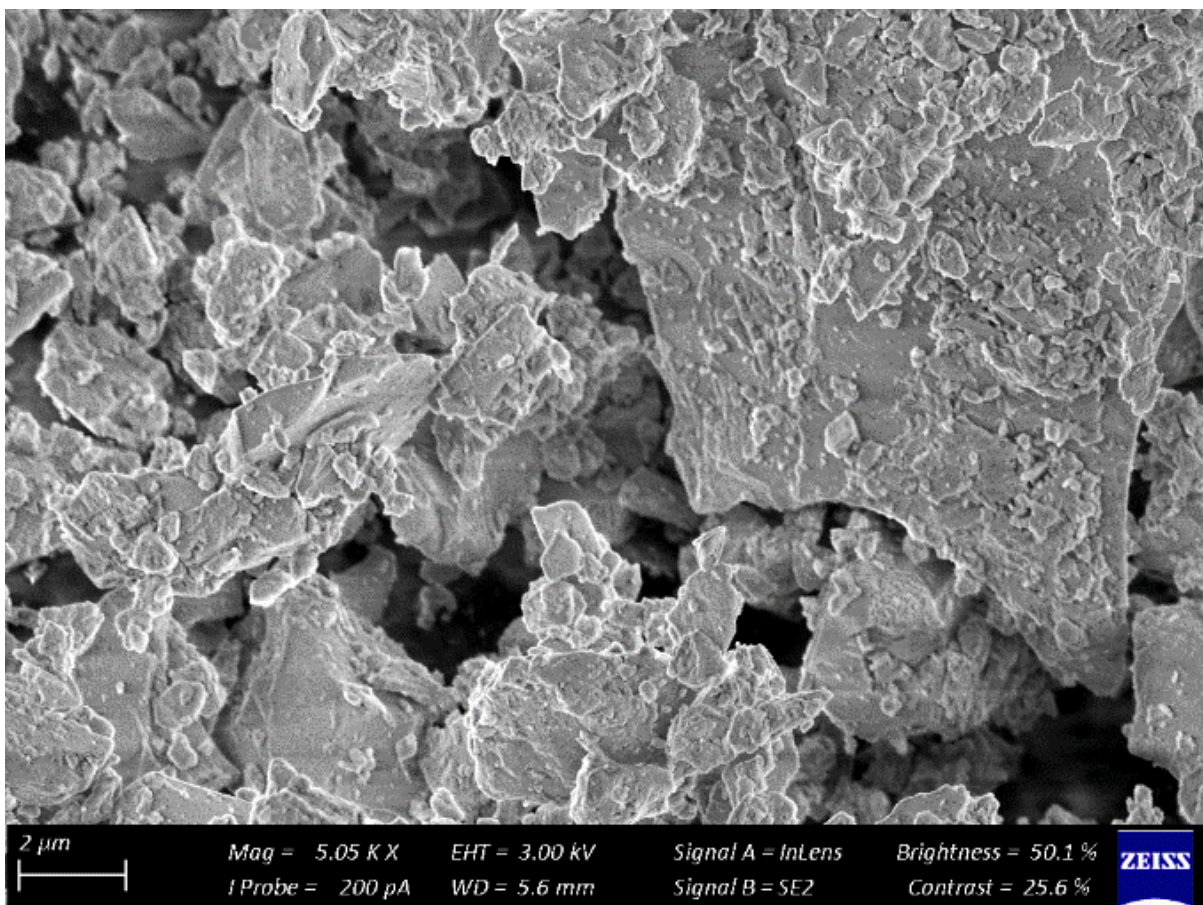
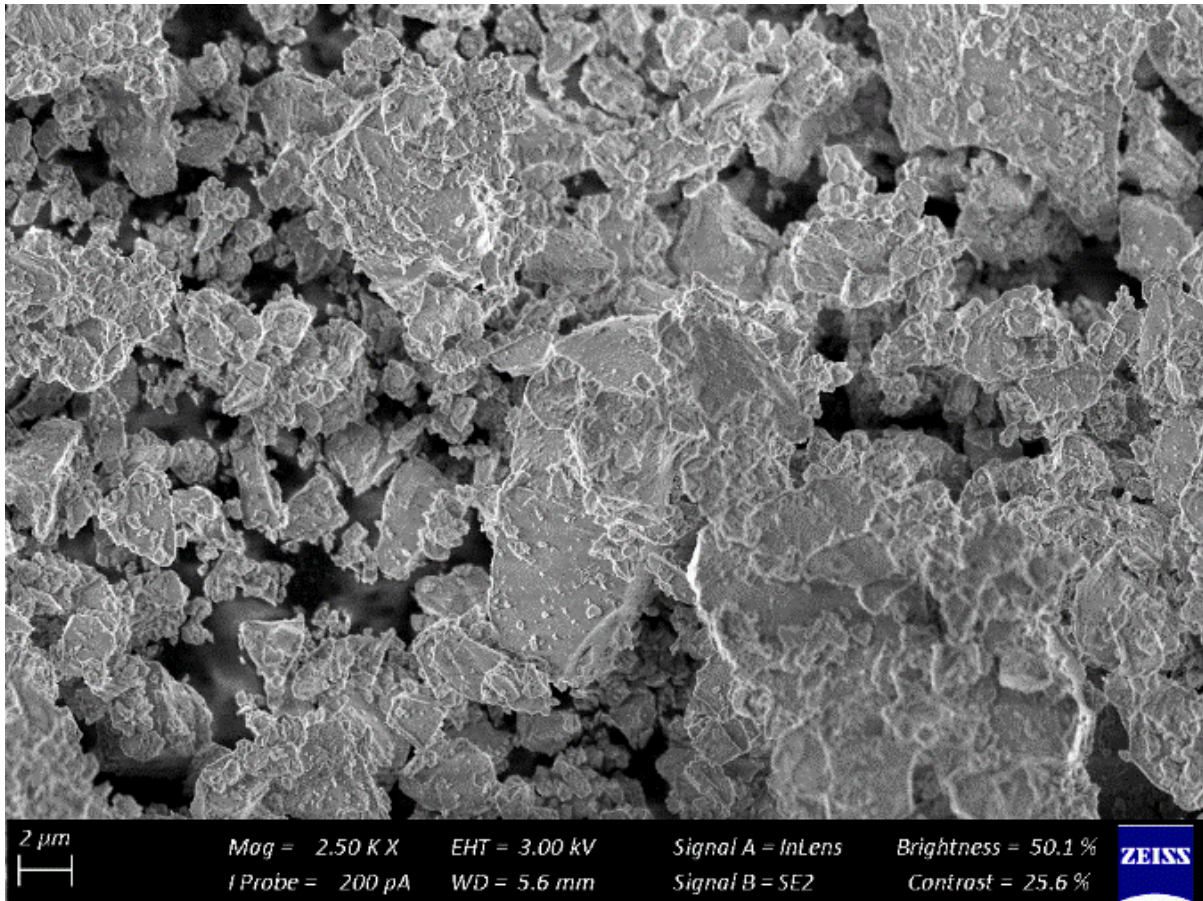




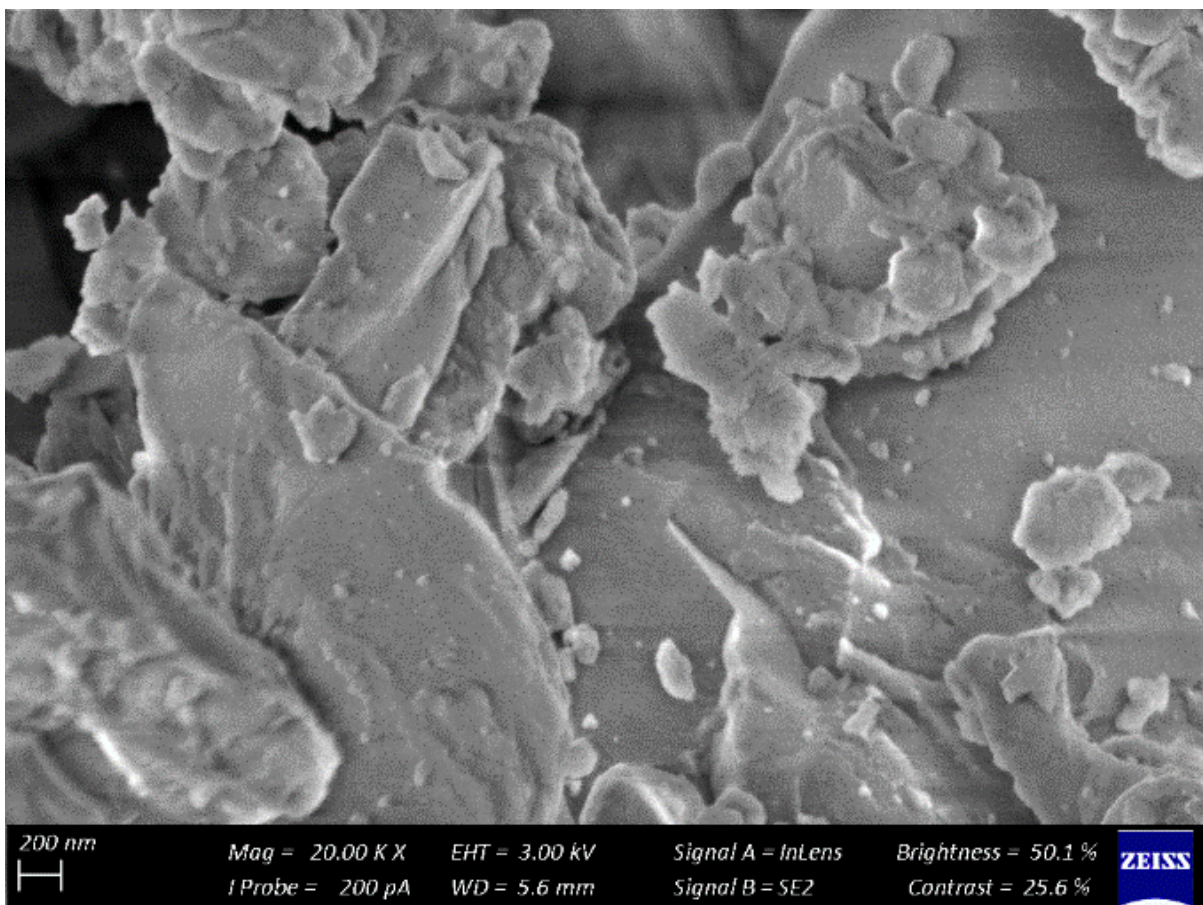
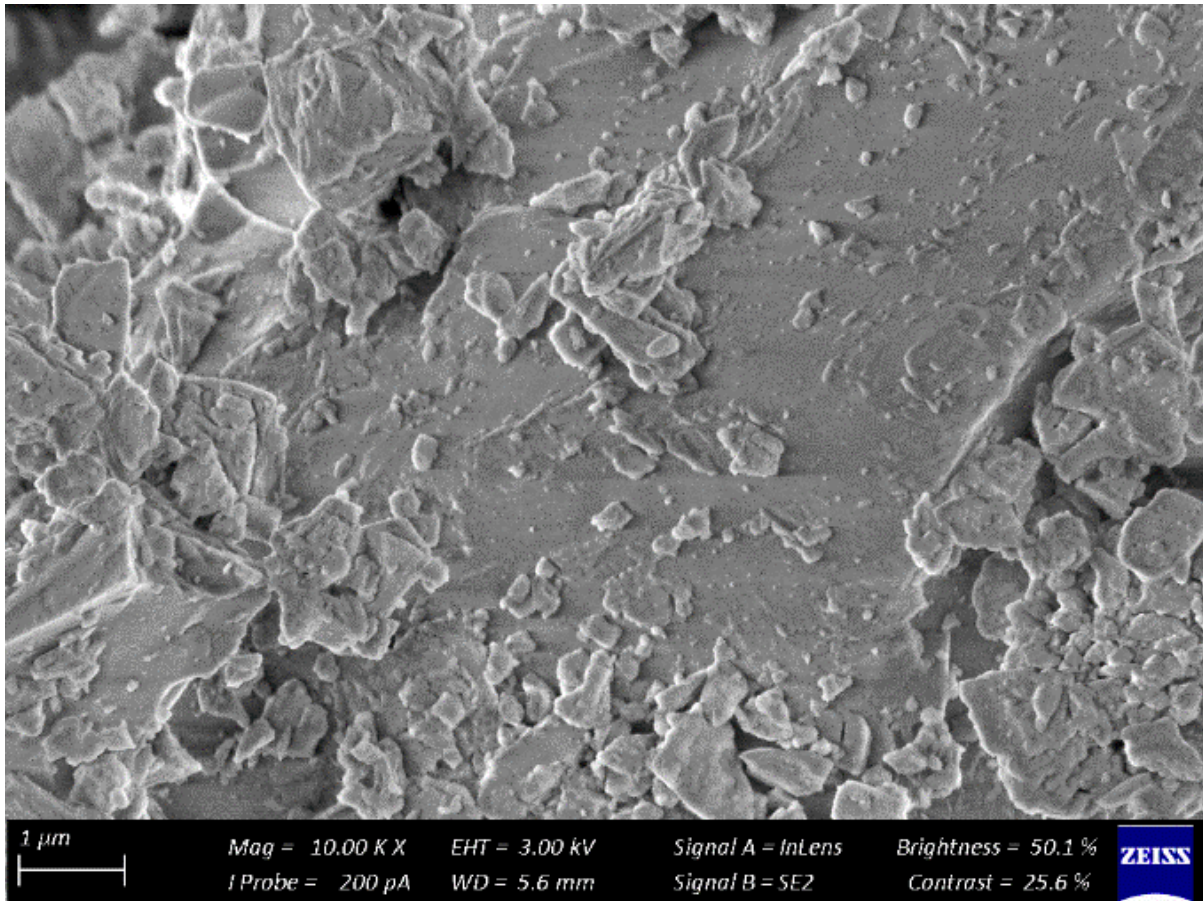
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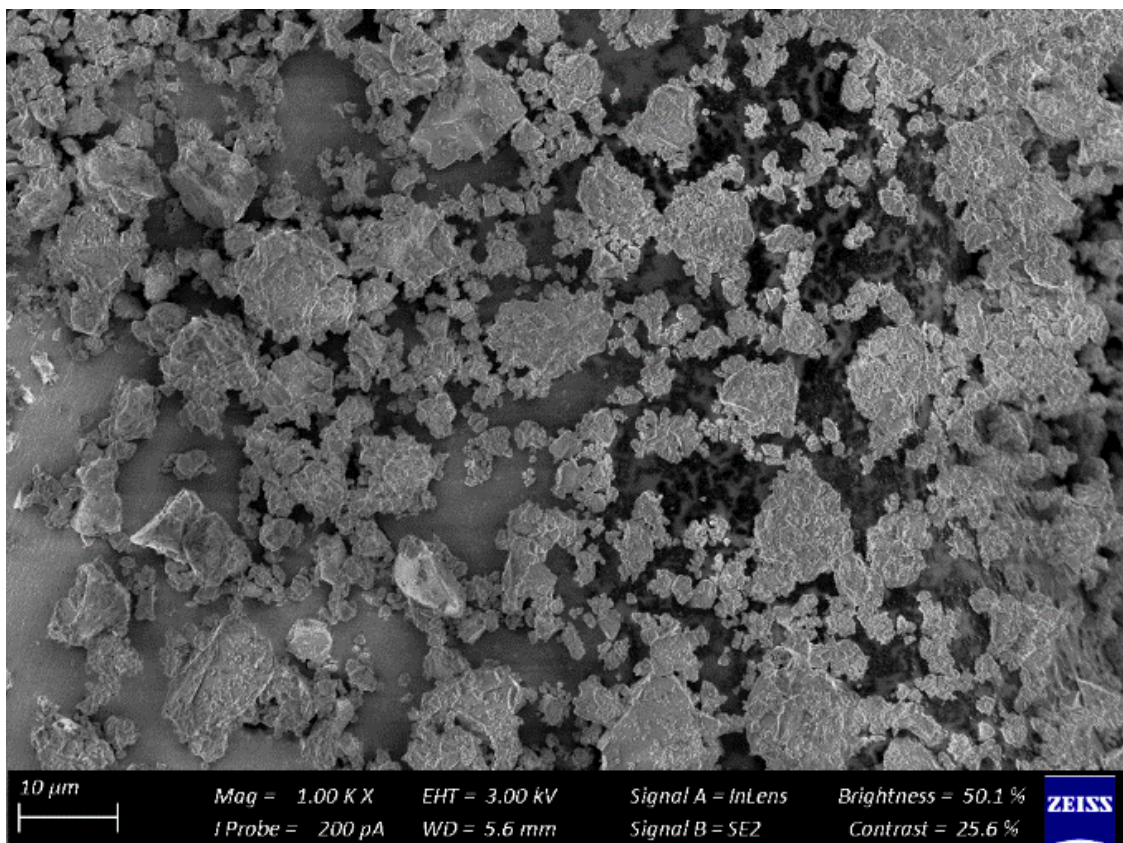
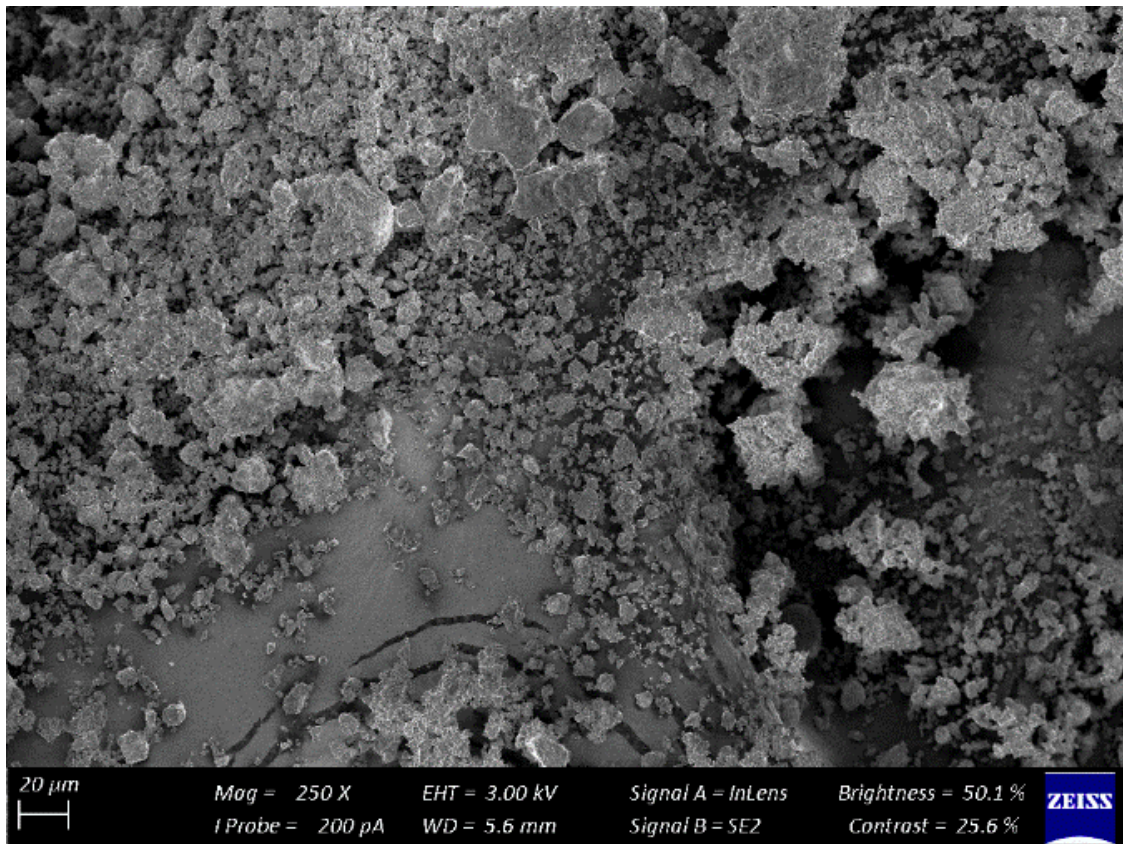




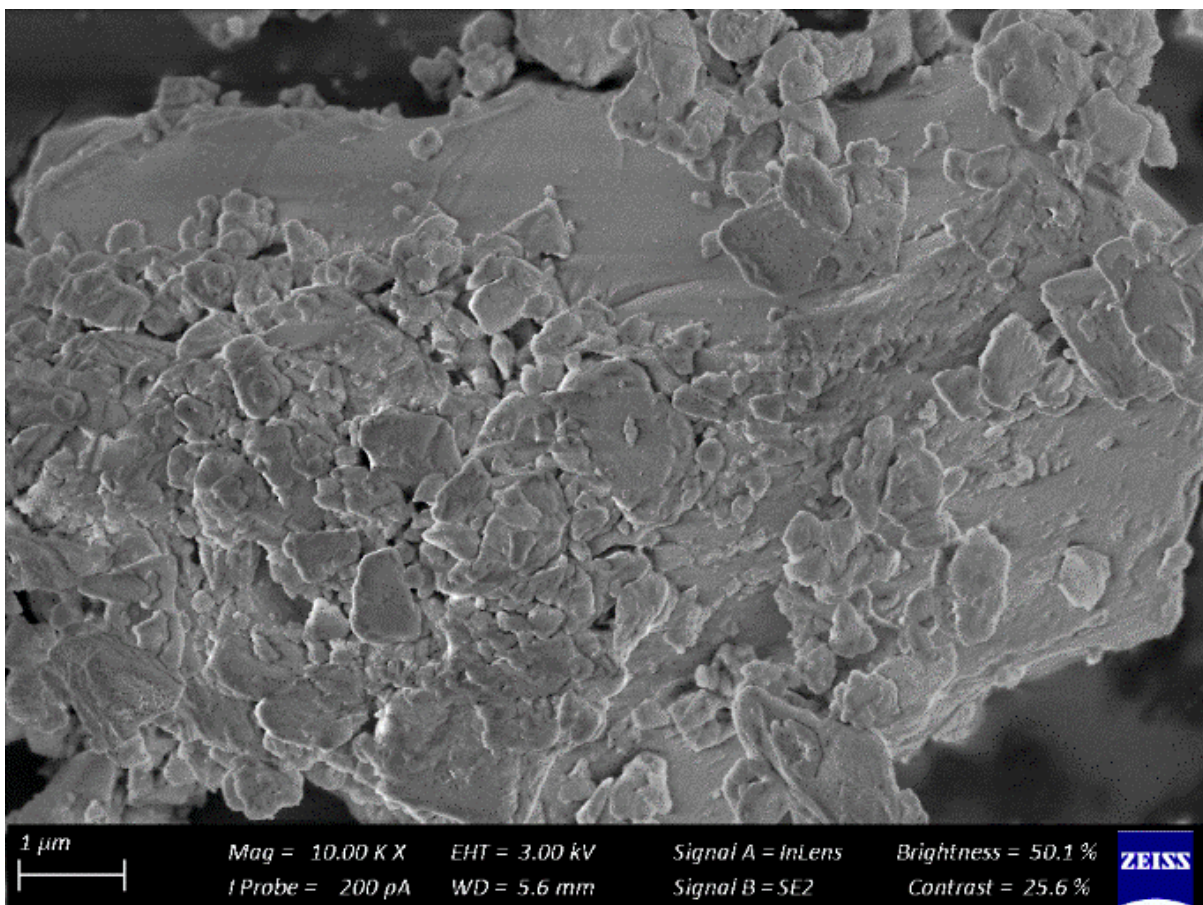
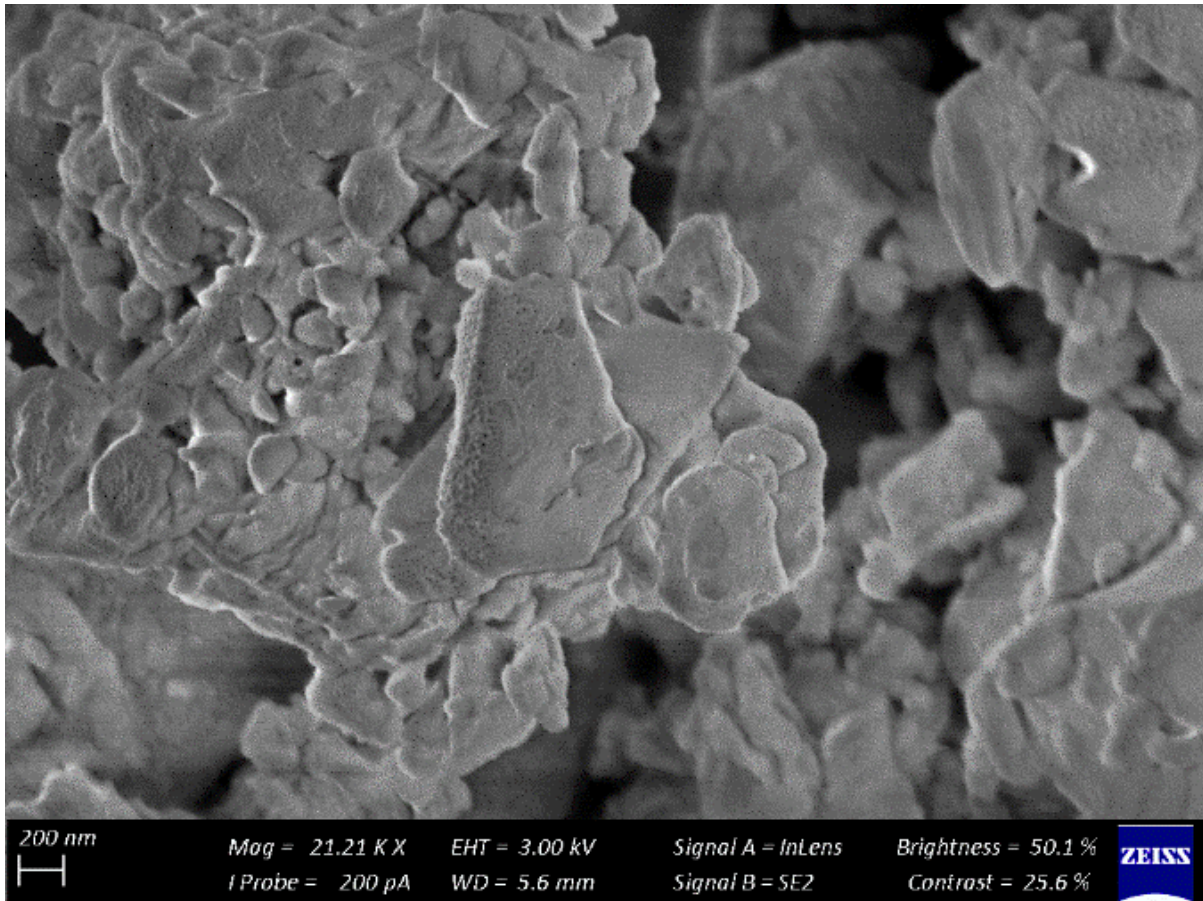




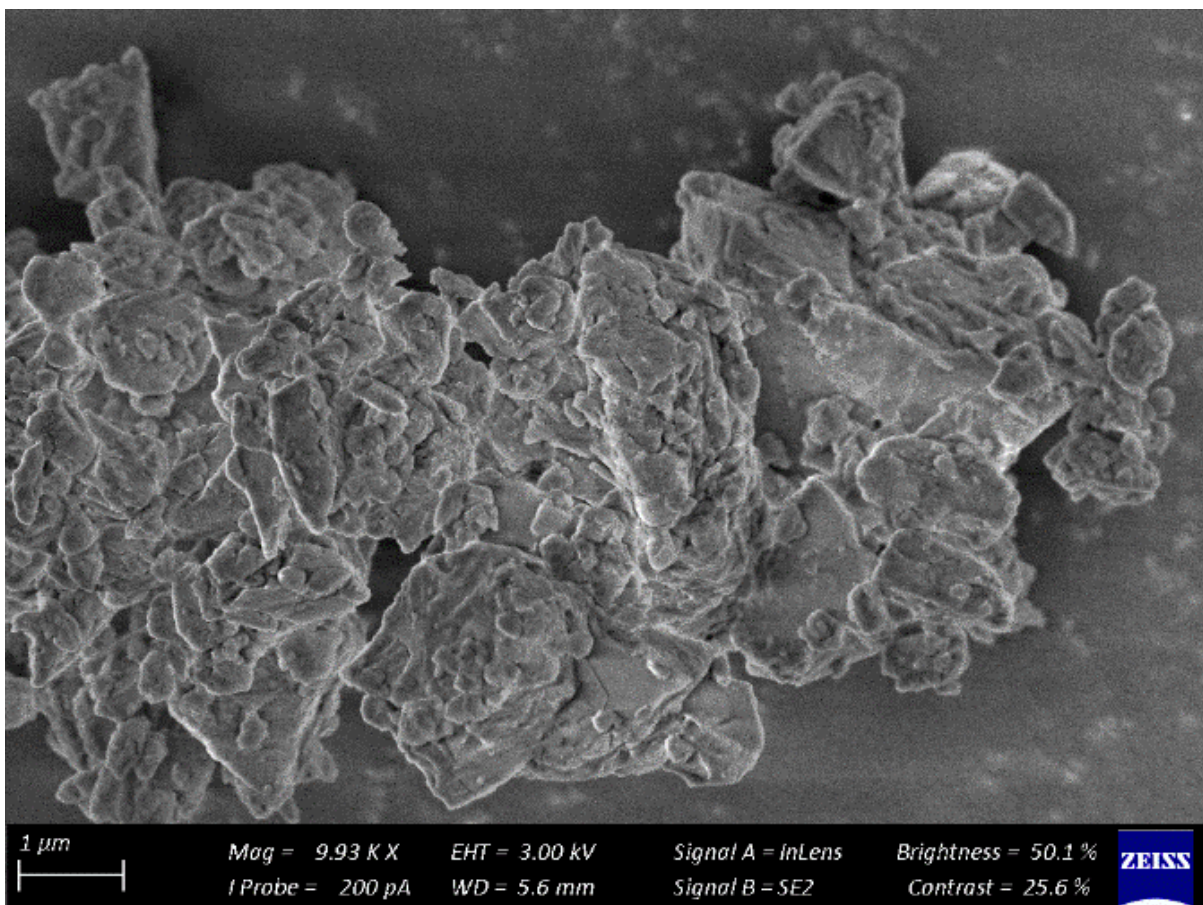
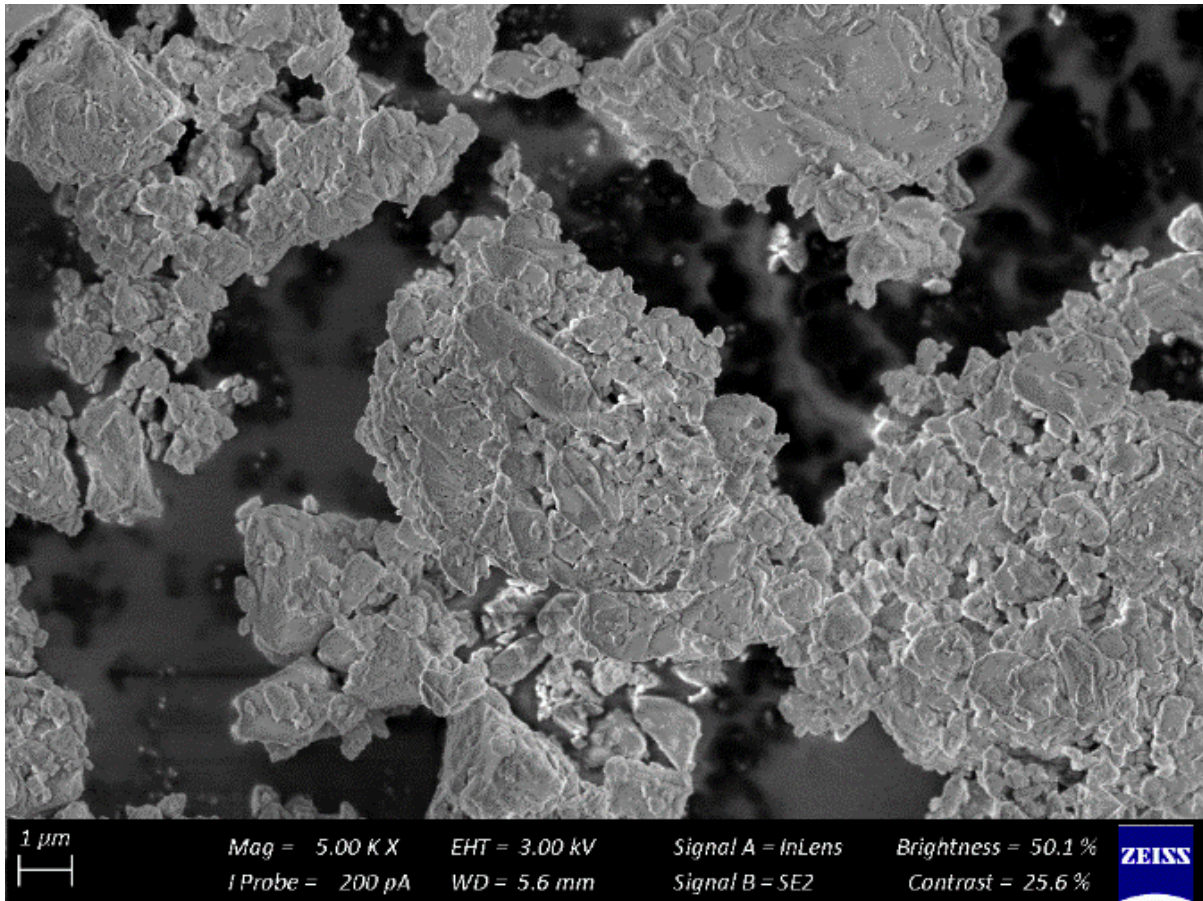
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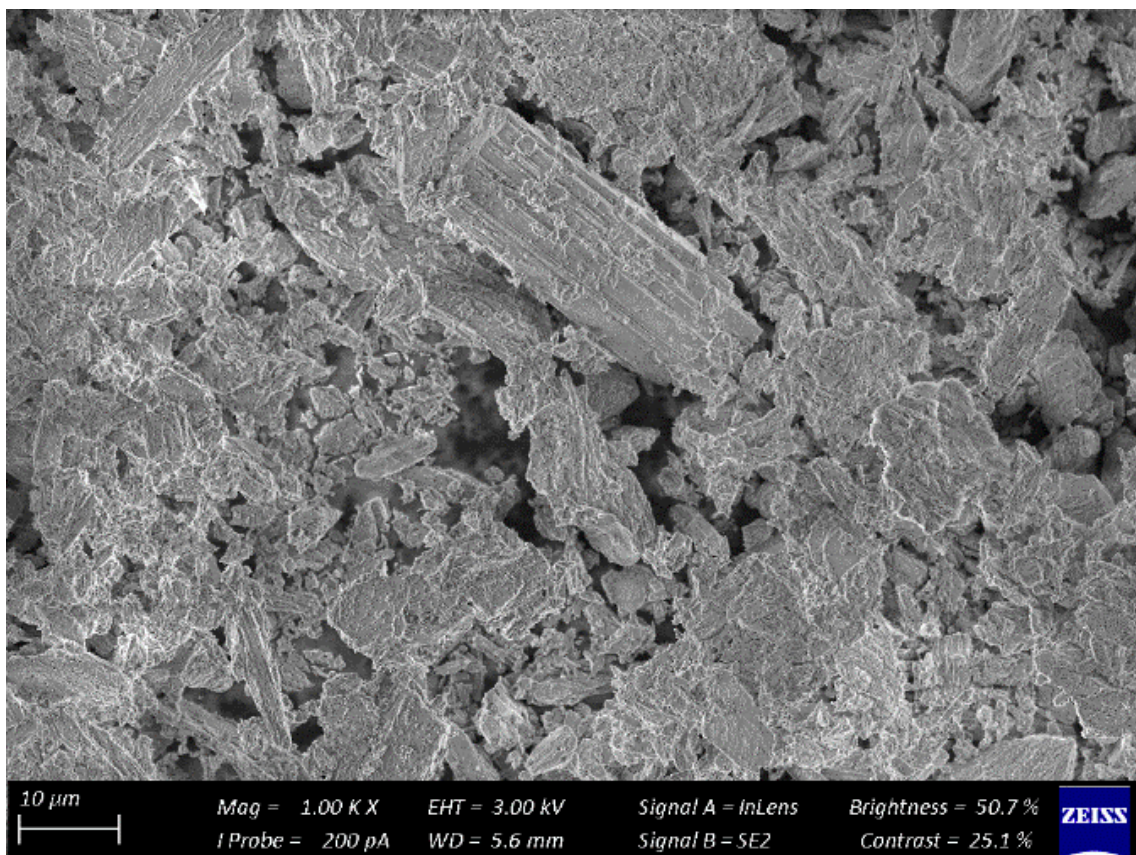




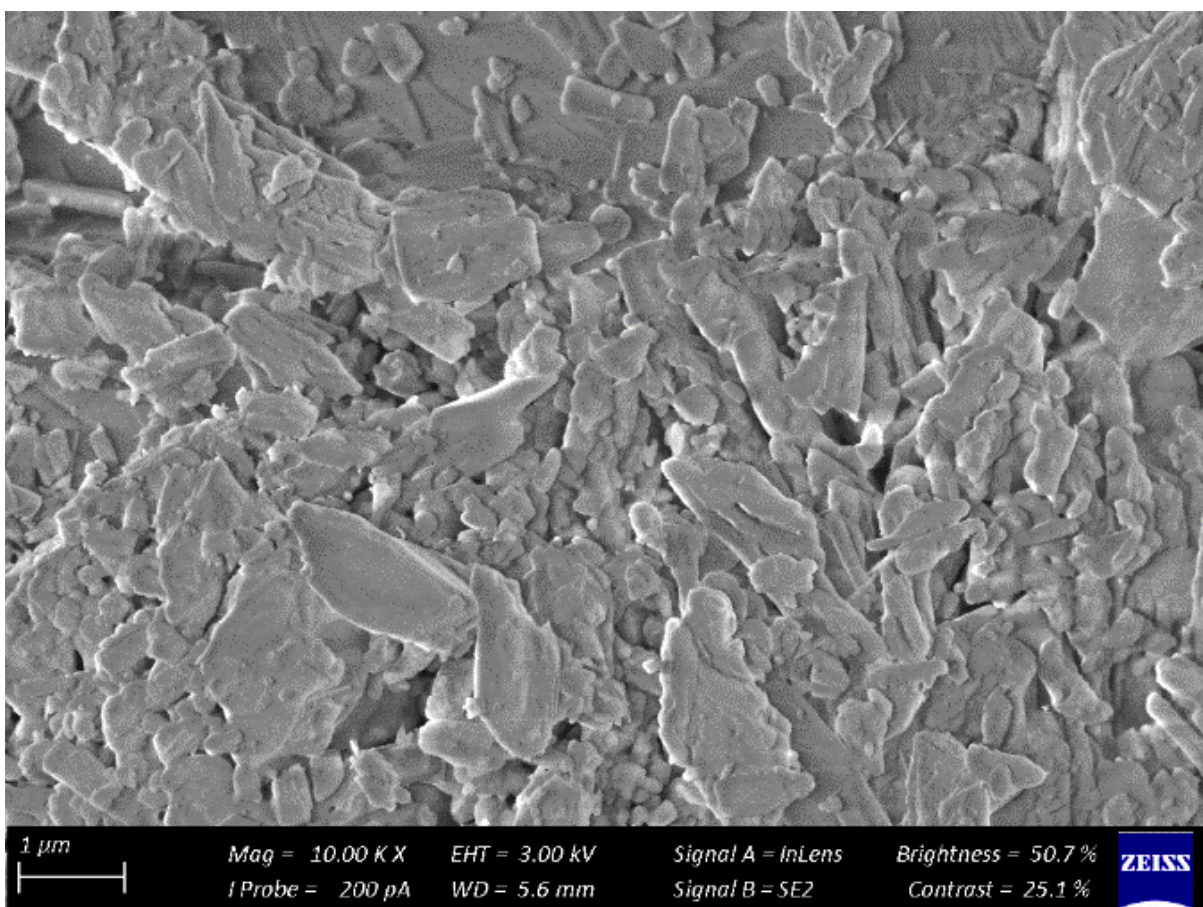
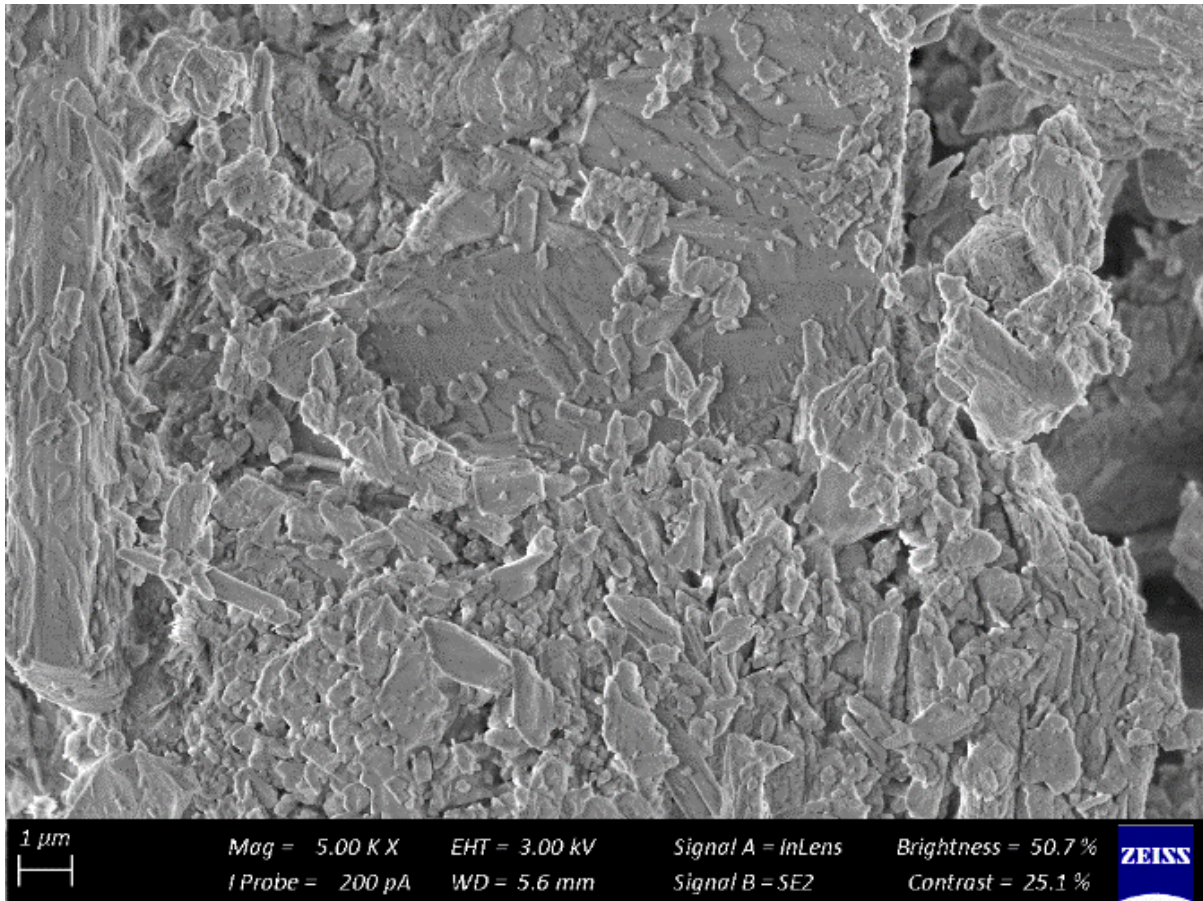




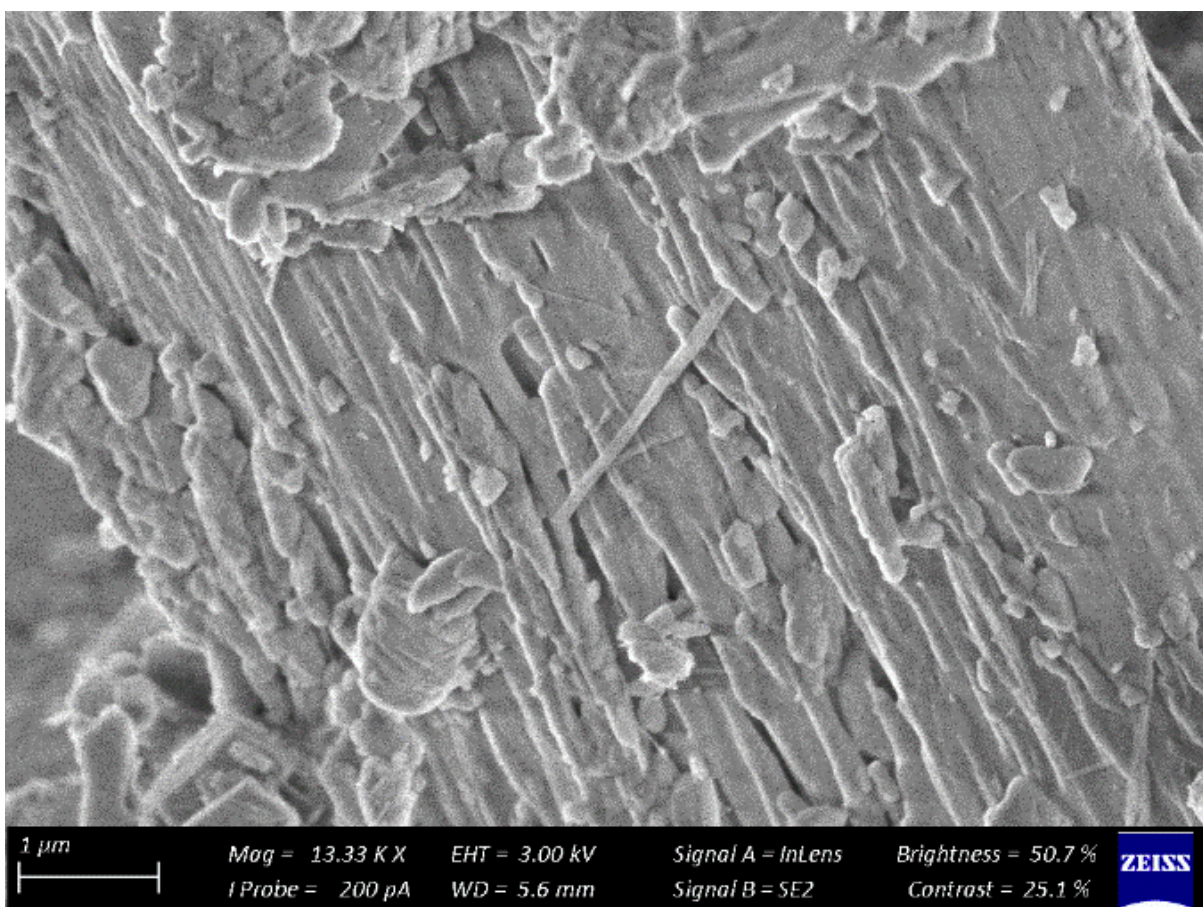
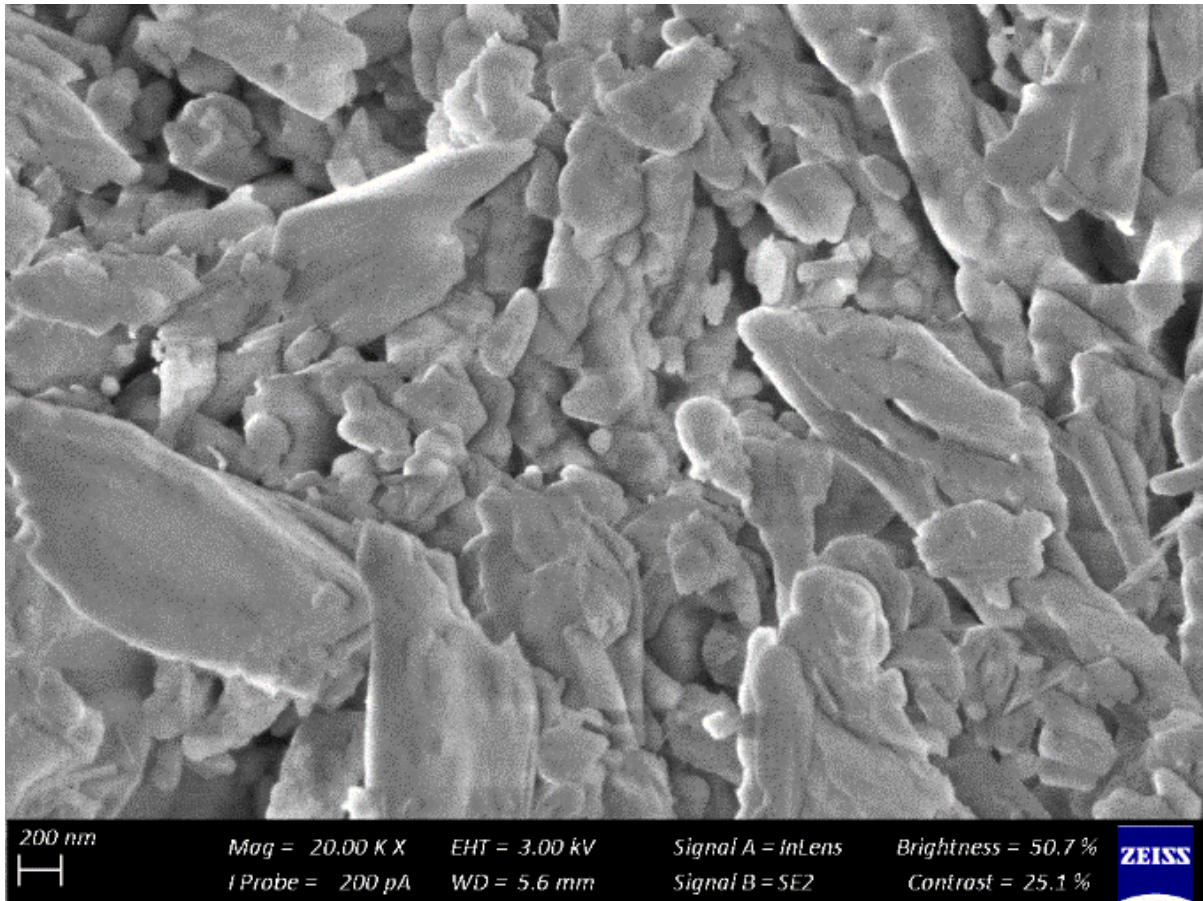
#### 8.4. SEM images for G1 (Bassanite)



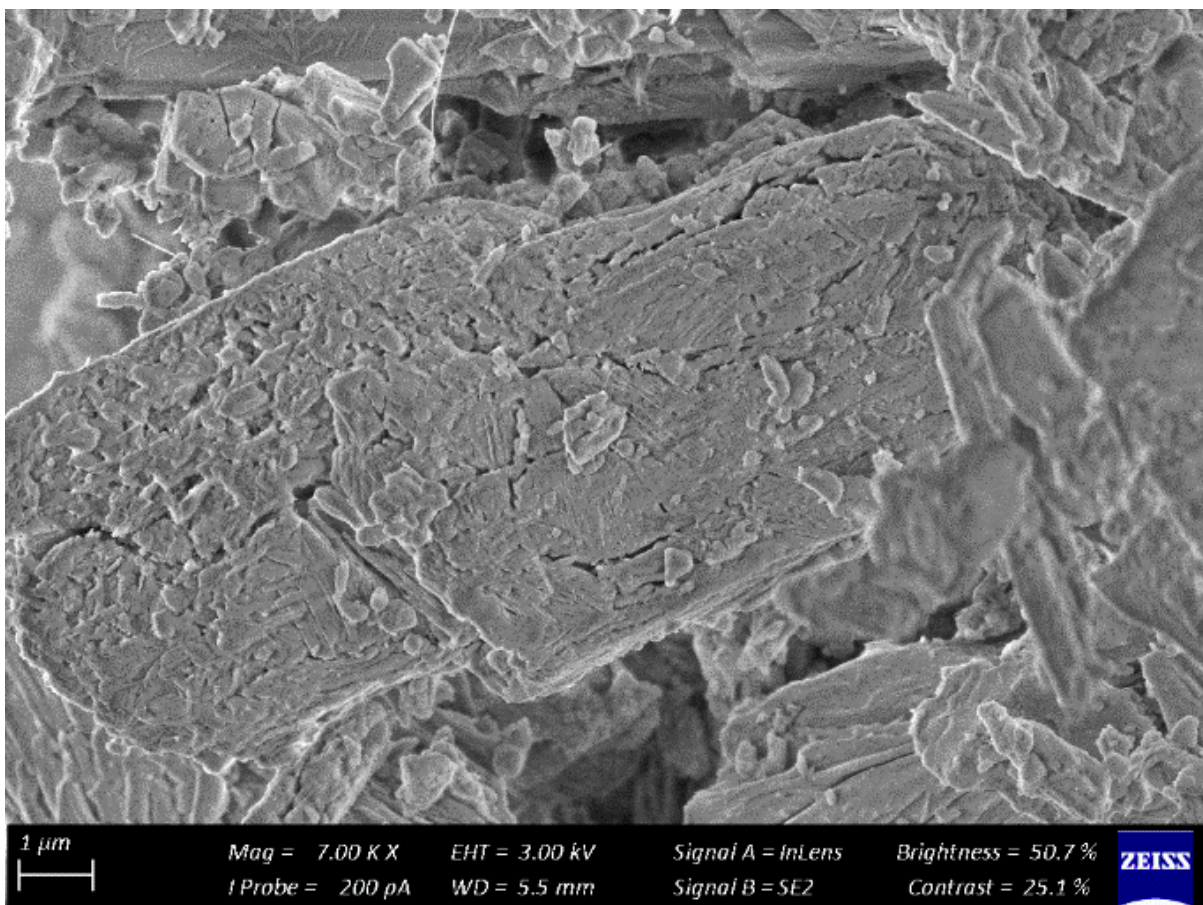
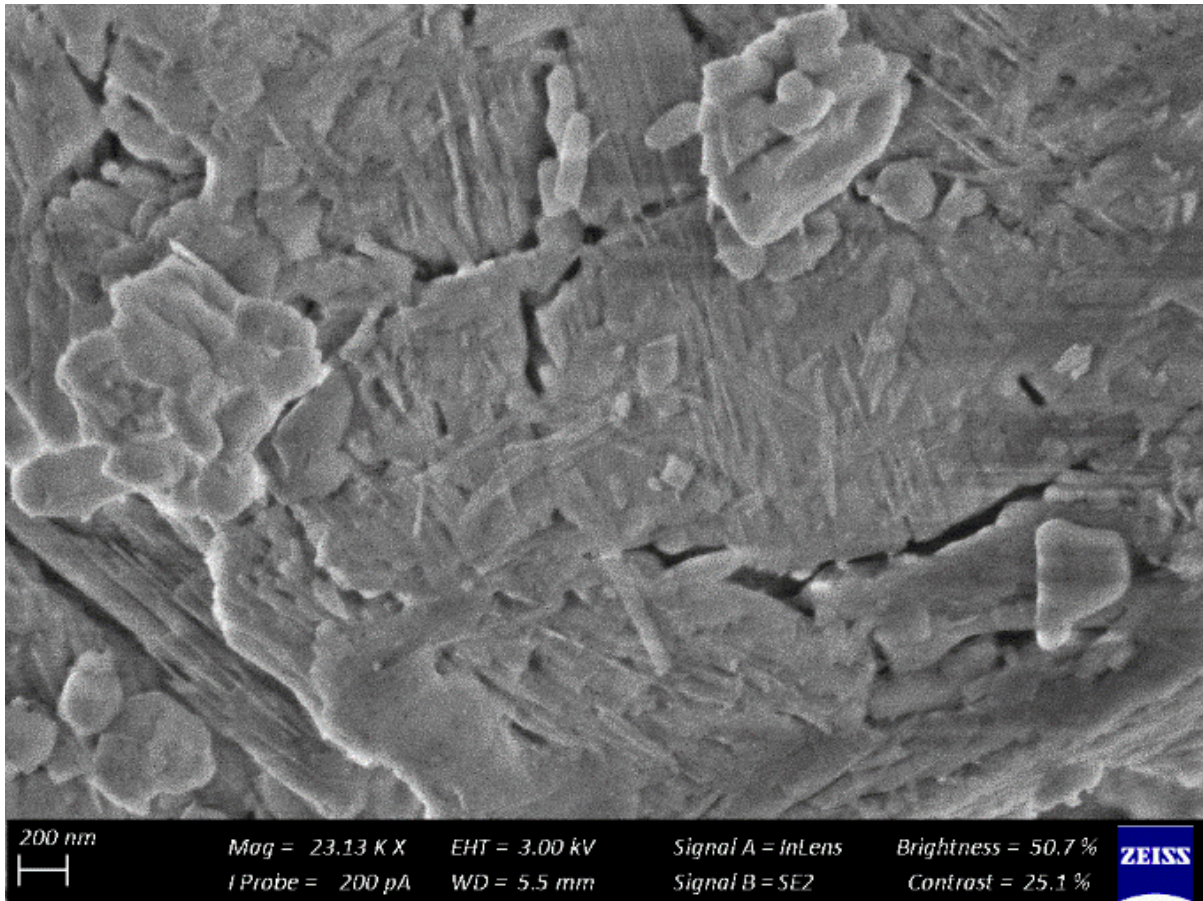




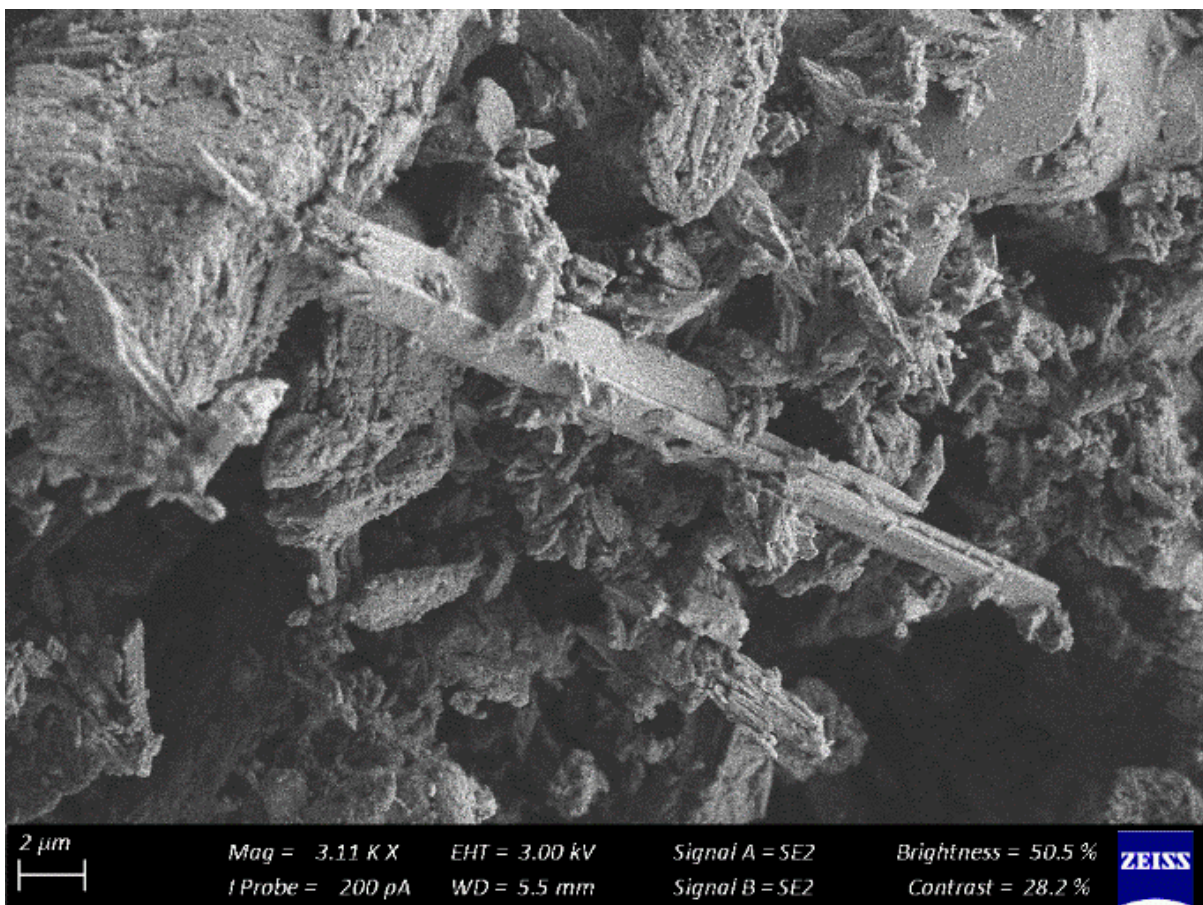
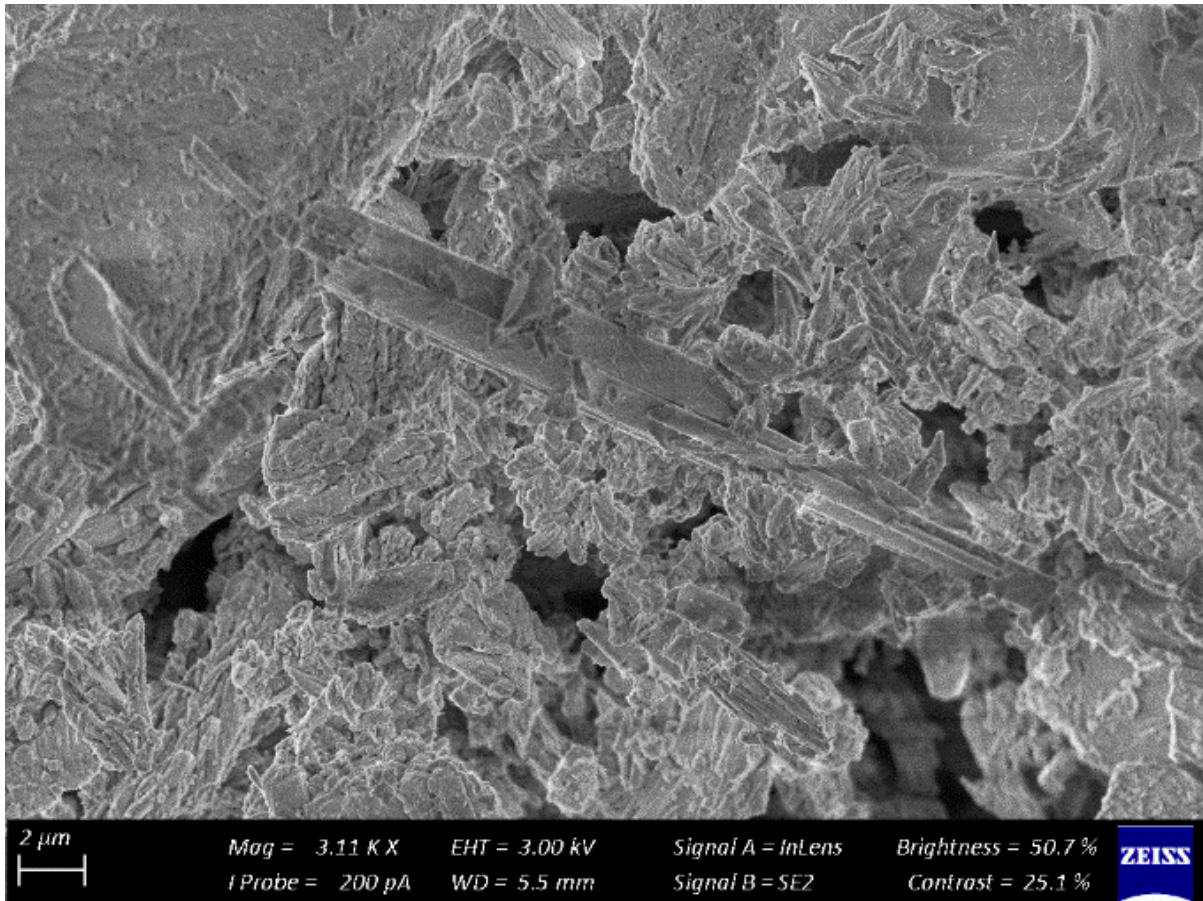




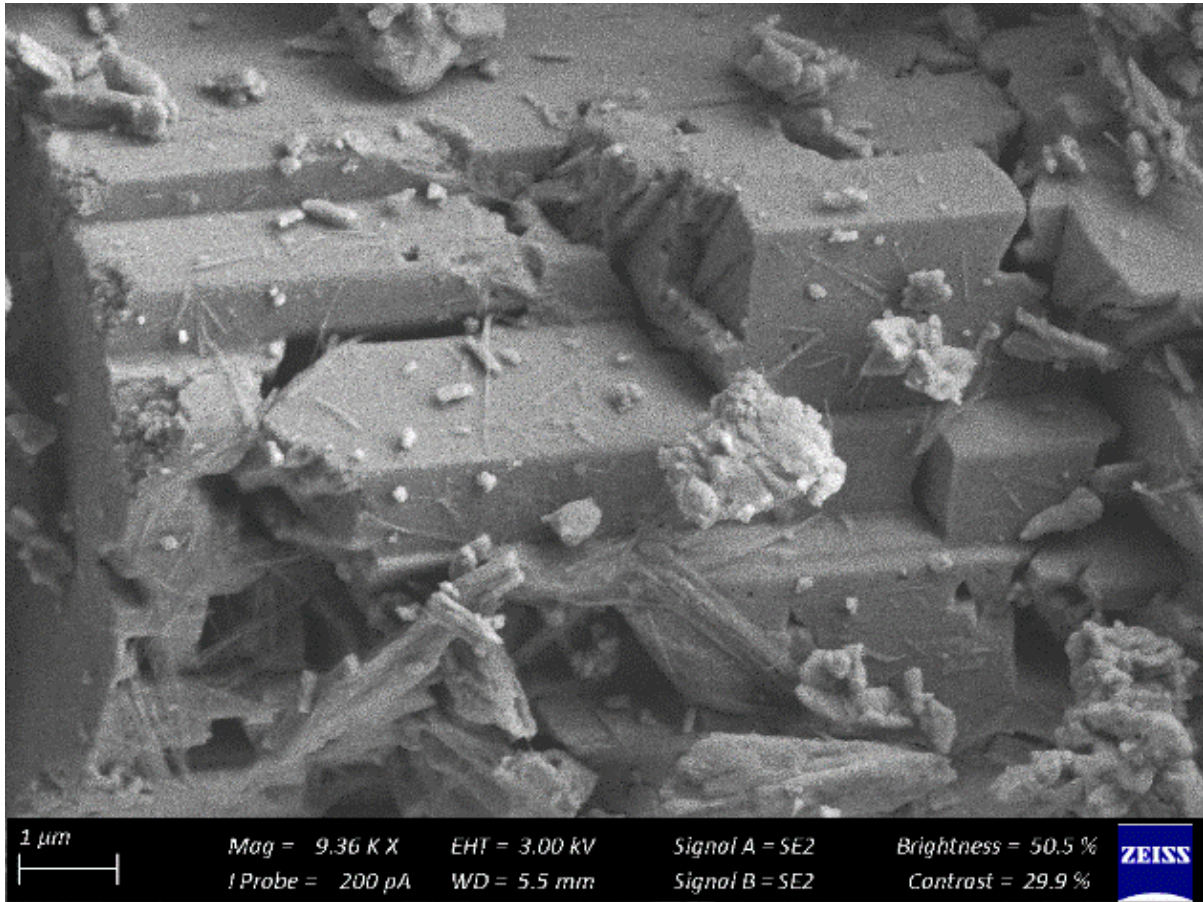




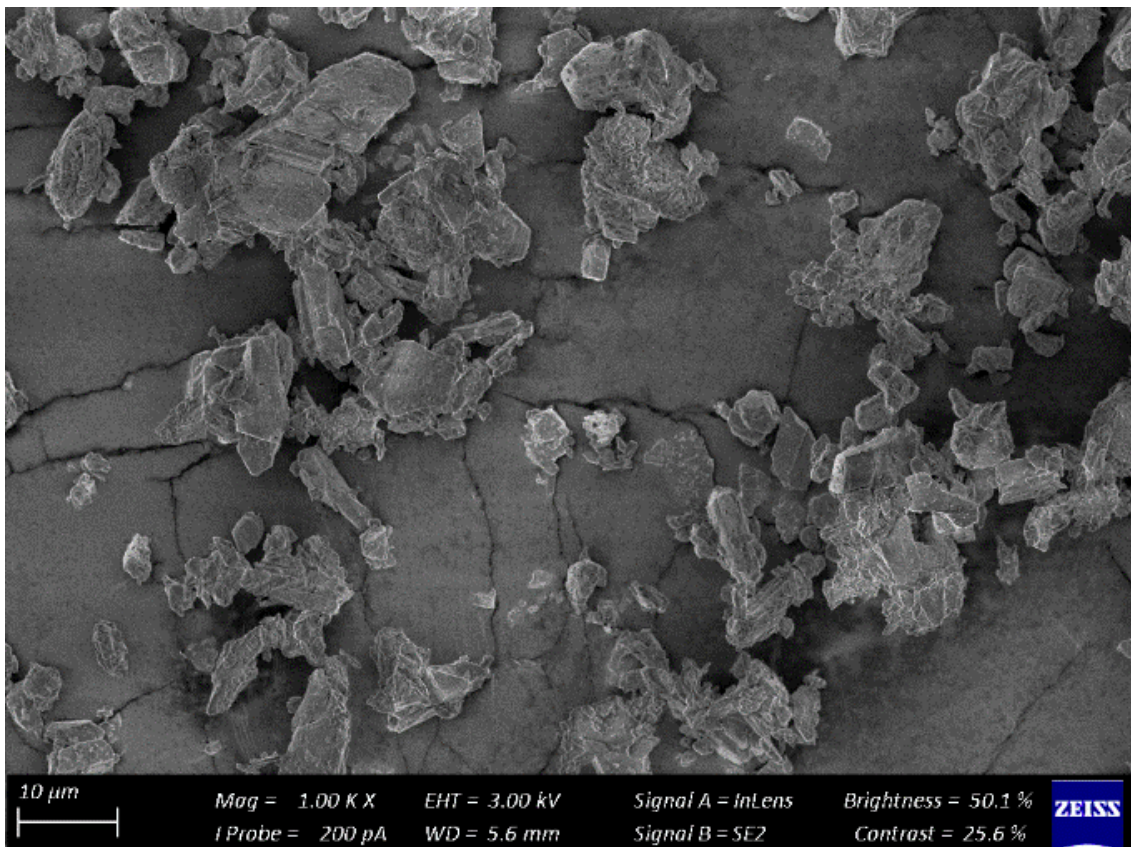
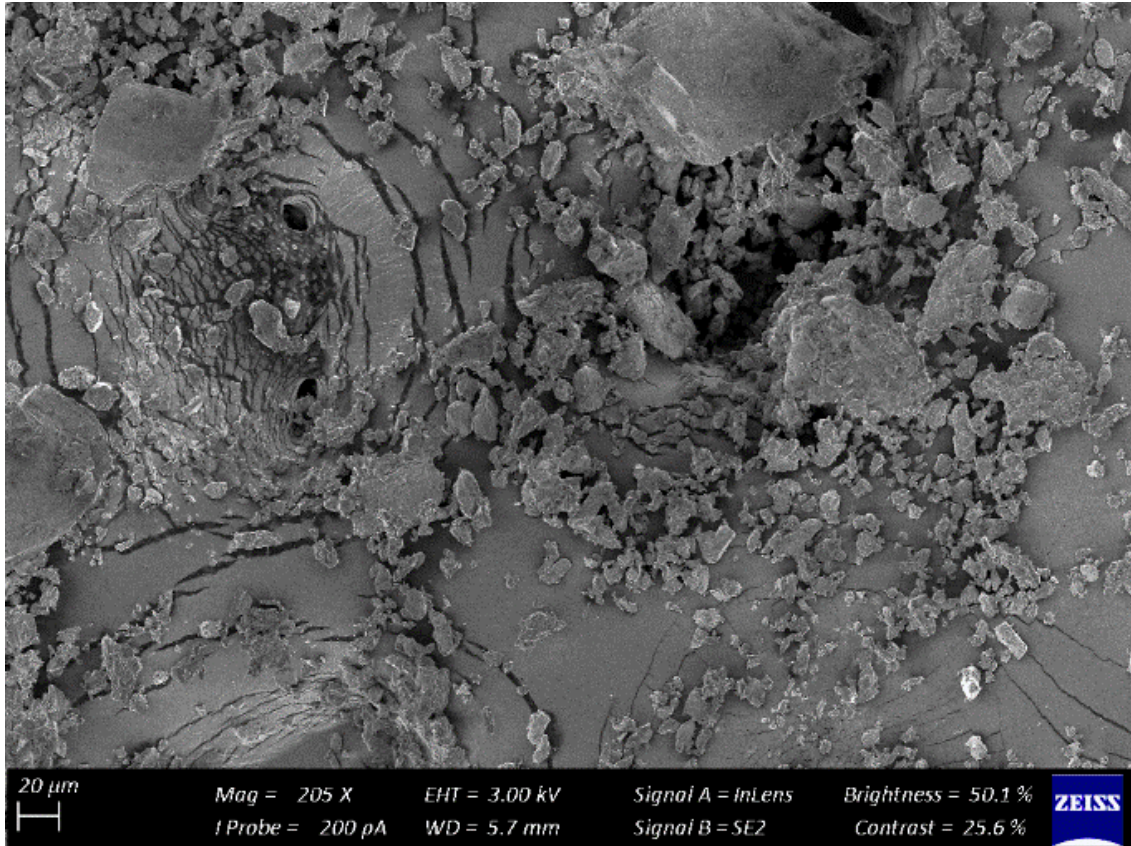




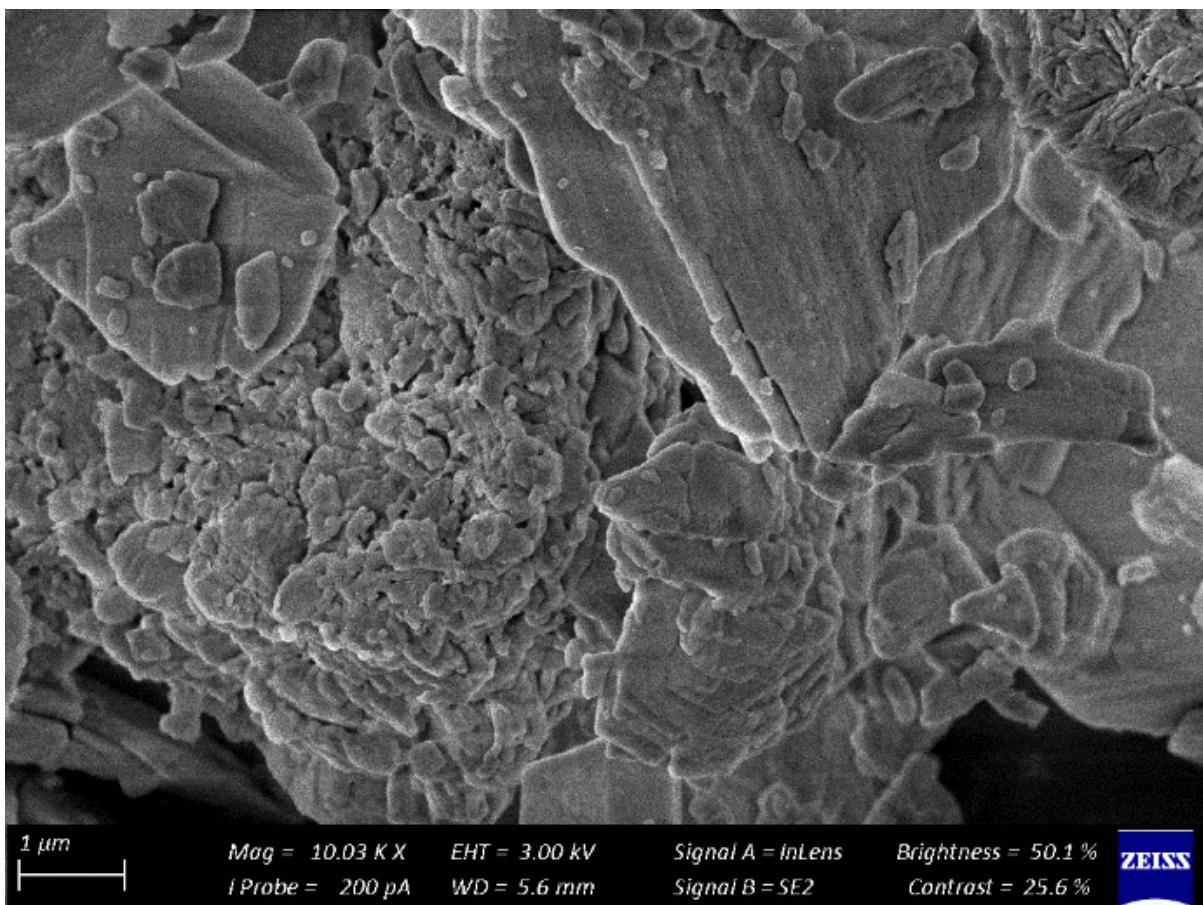
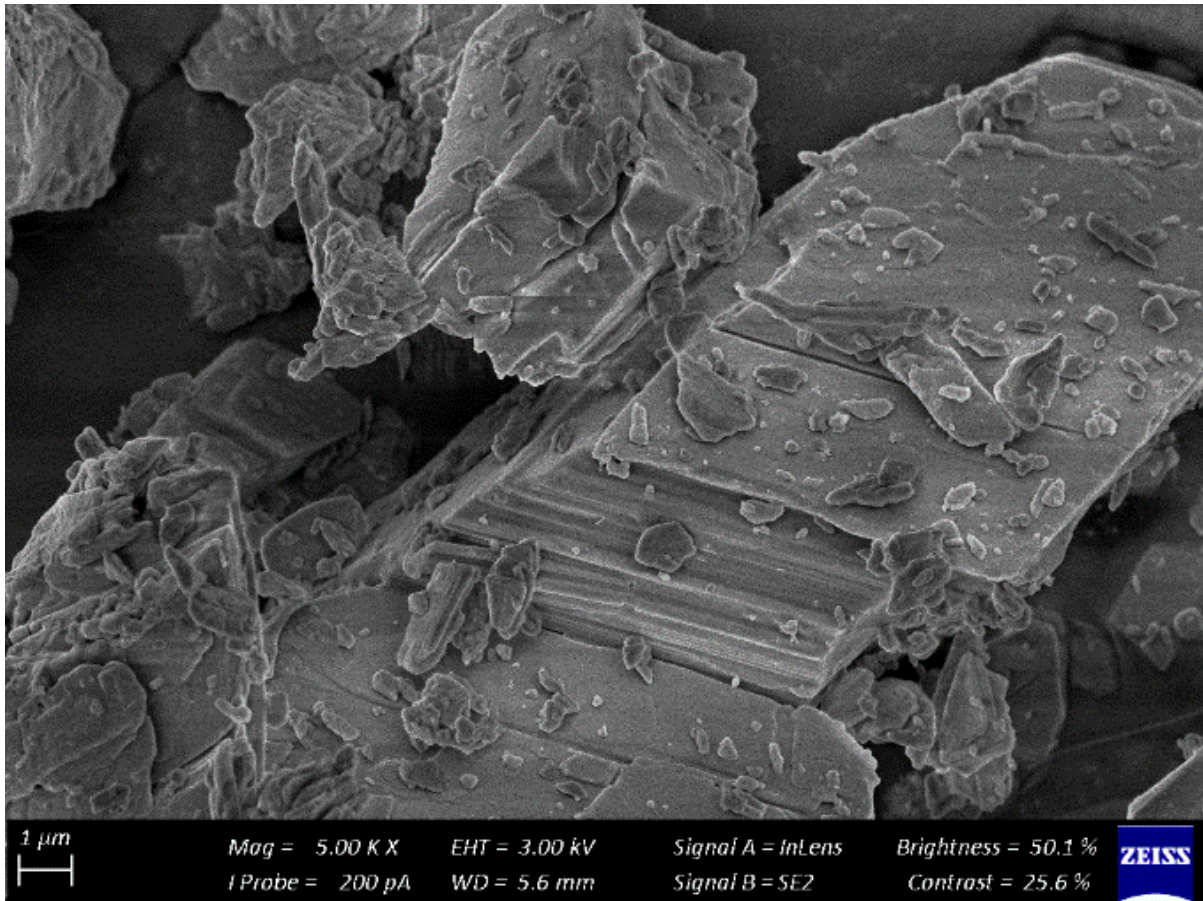




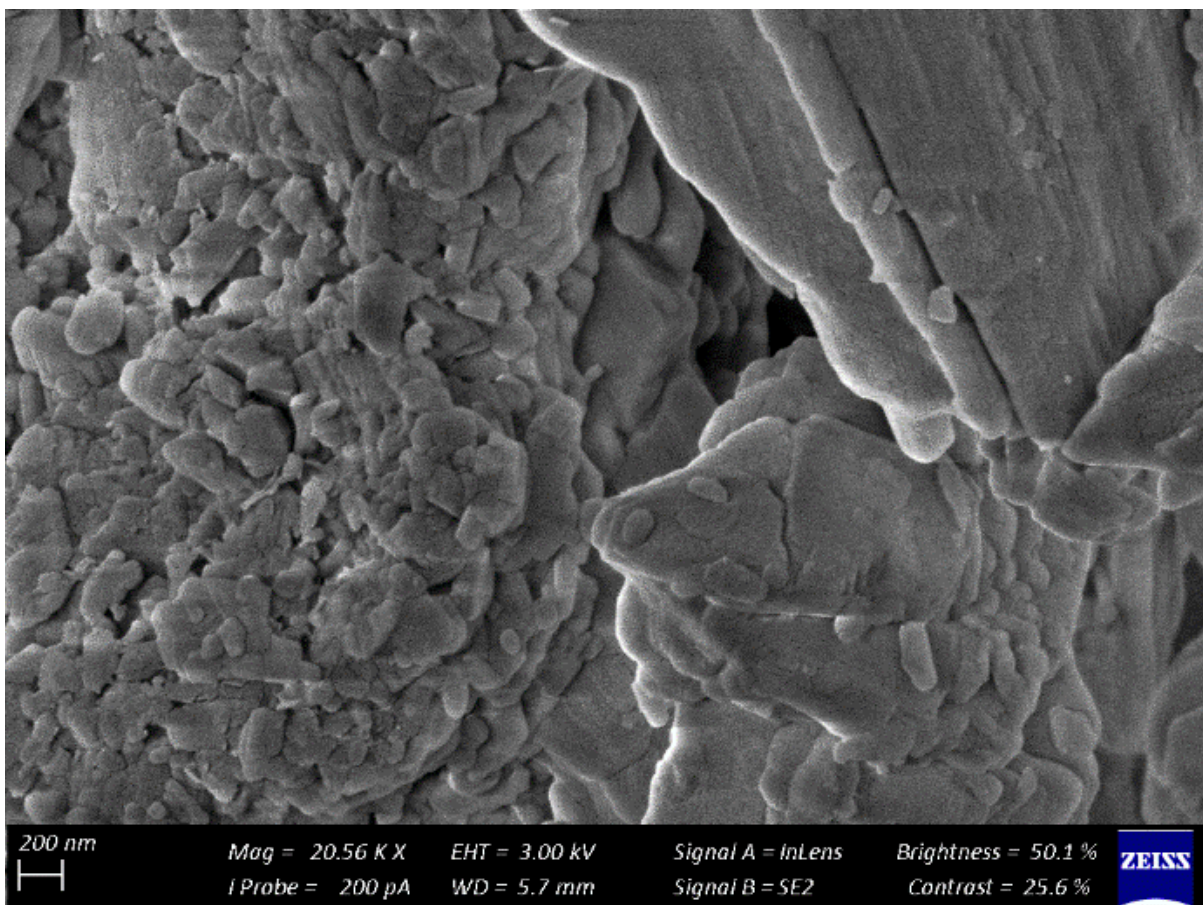
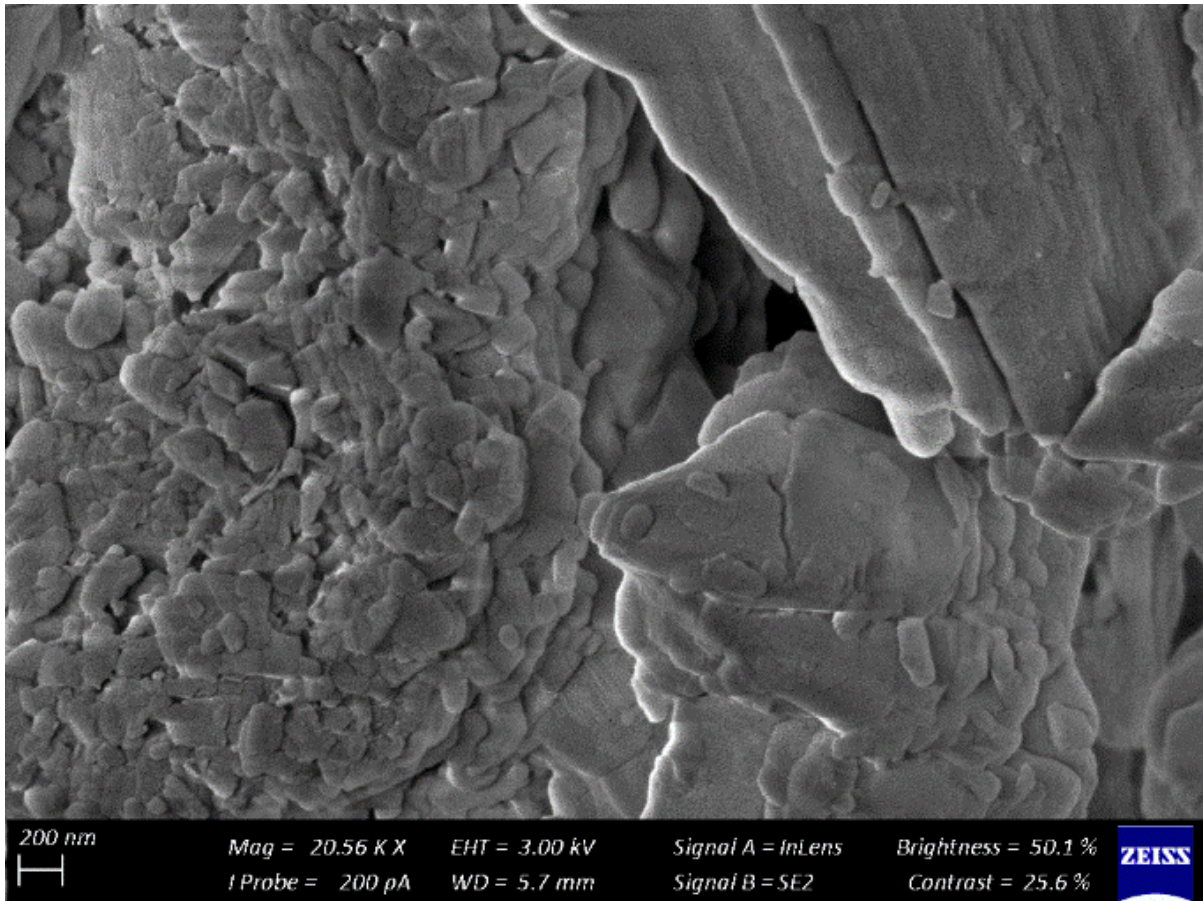
### 8.5. SEM images for G2 (Gypsum)



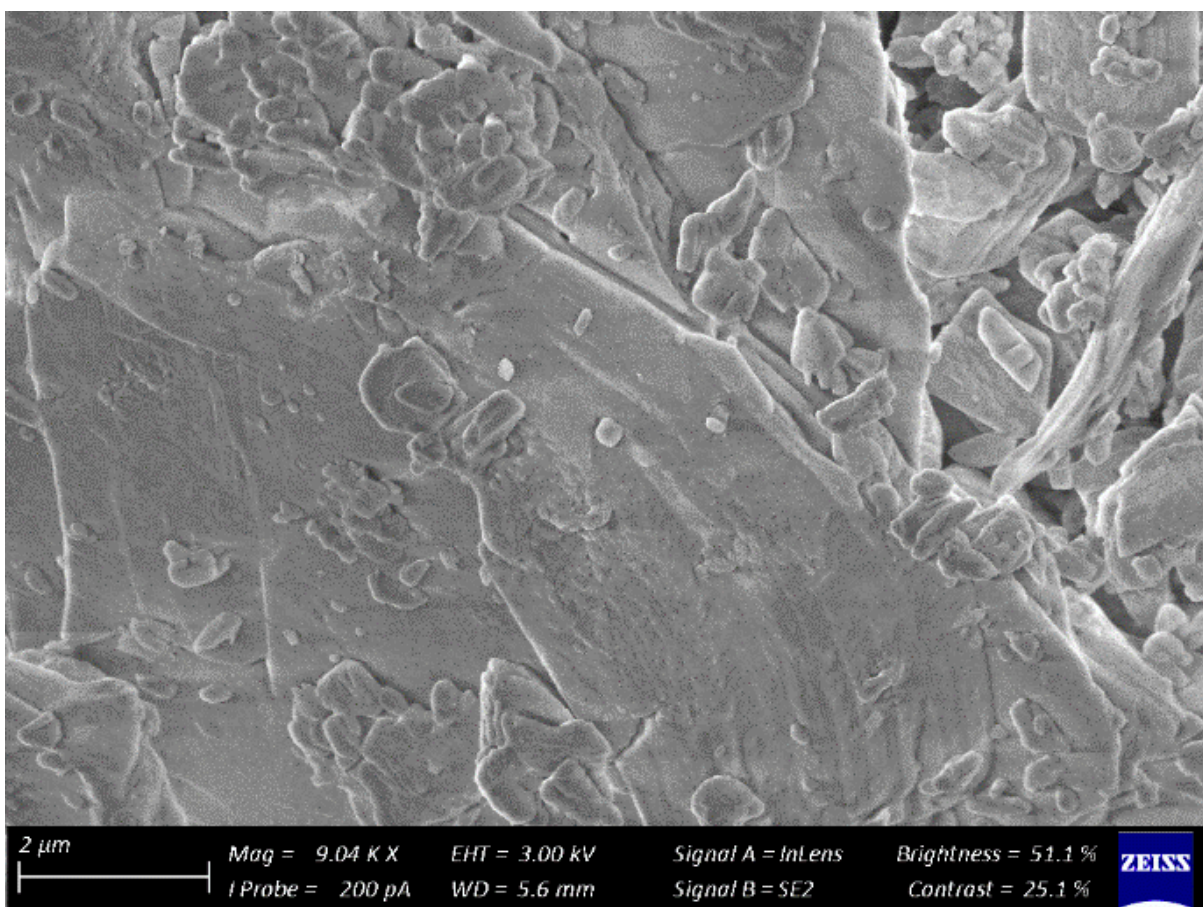
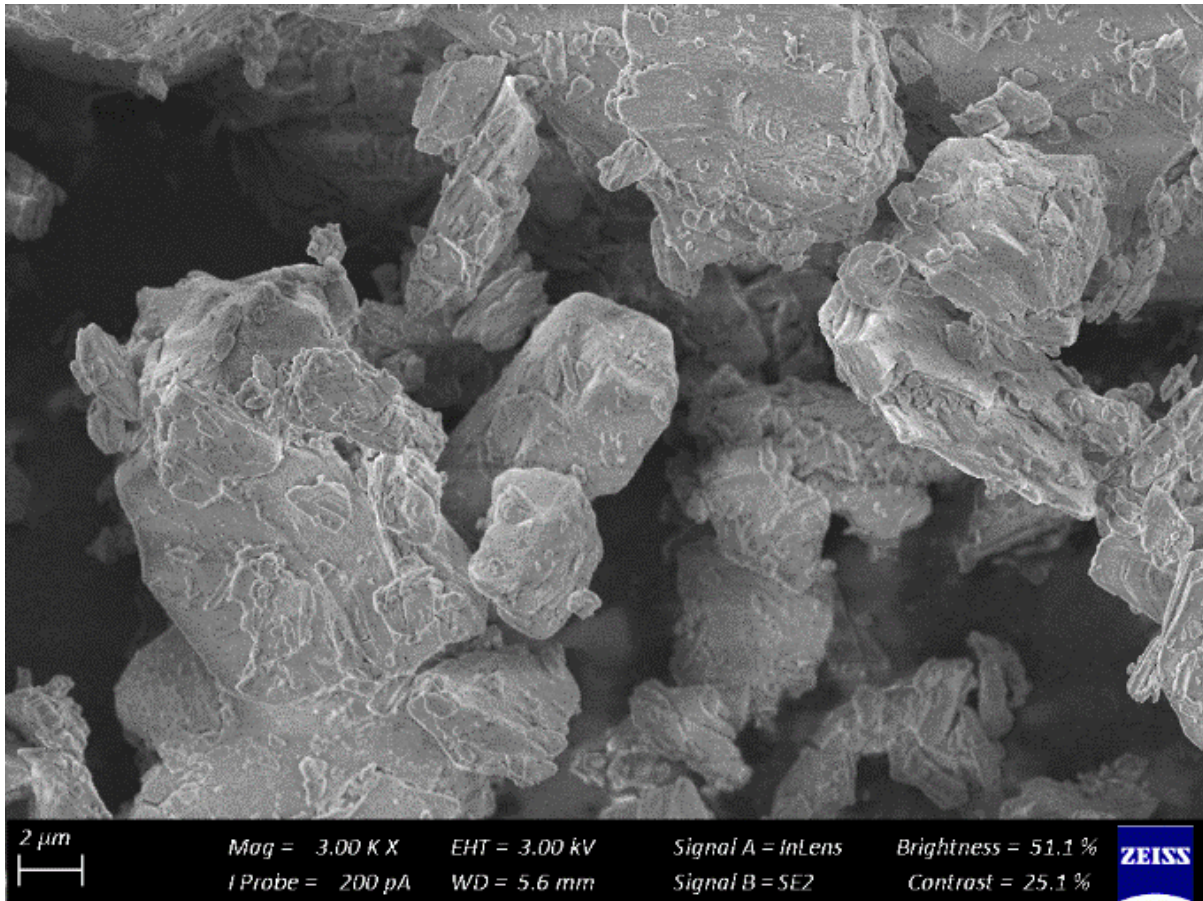






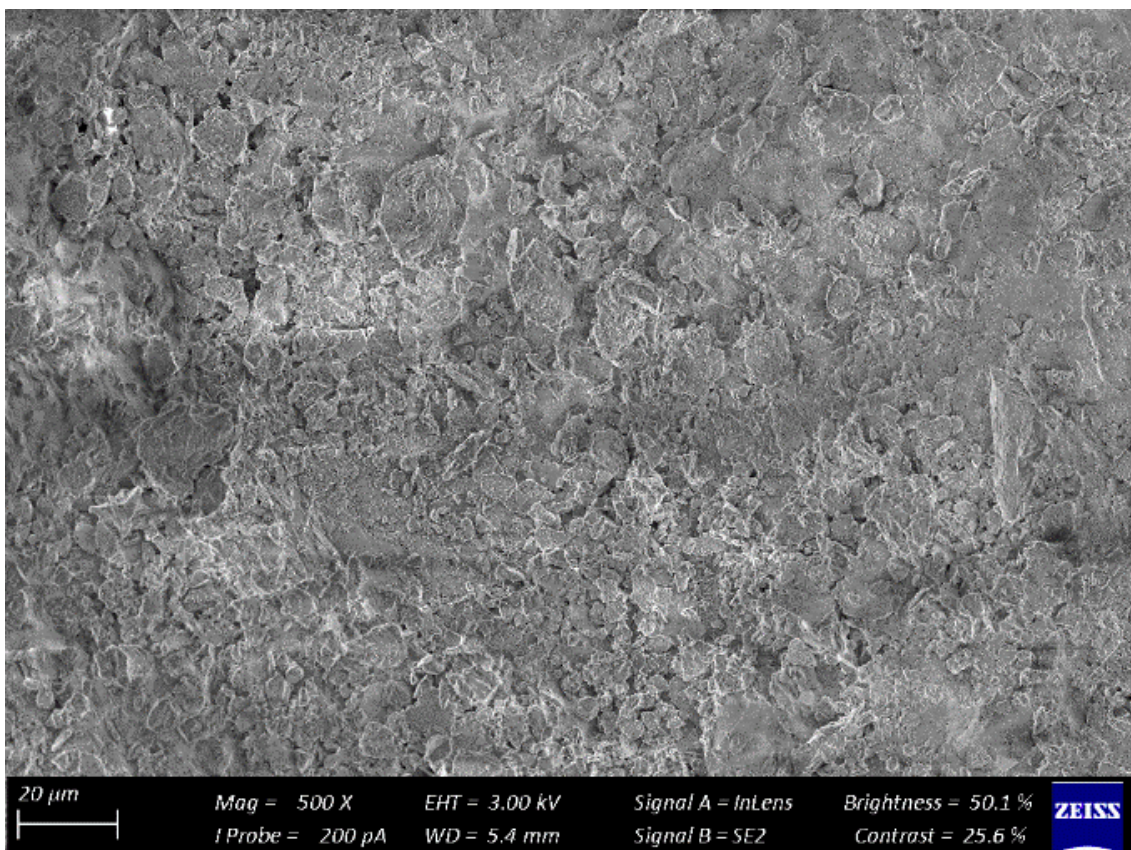
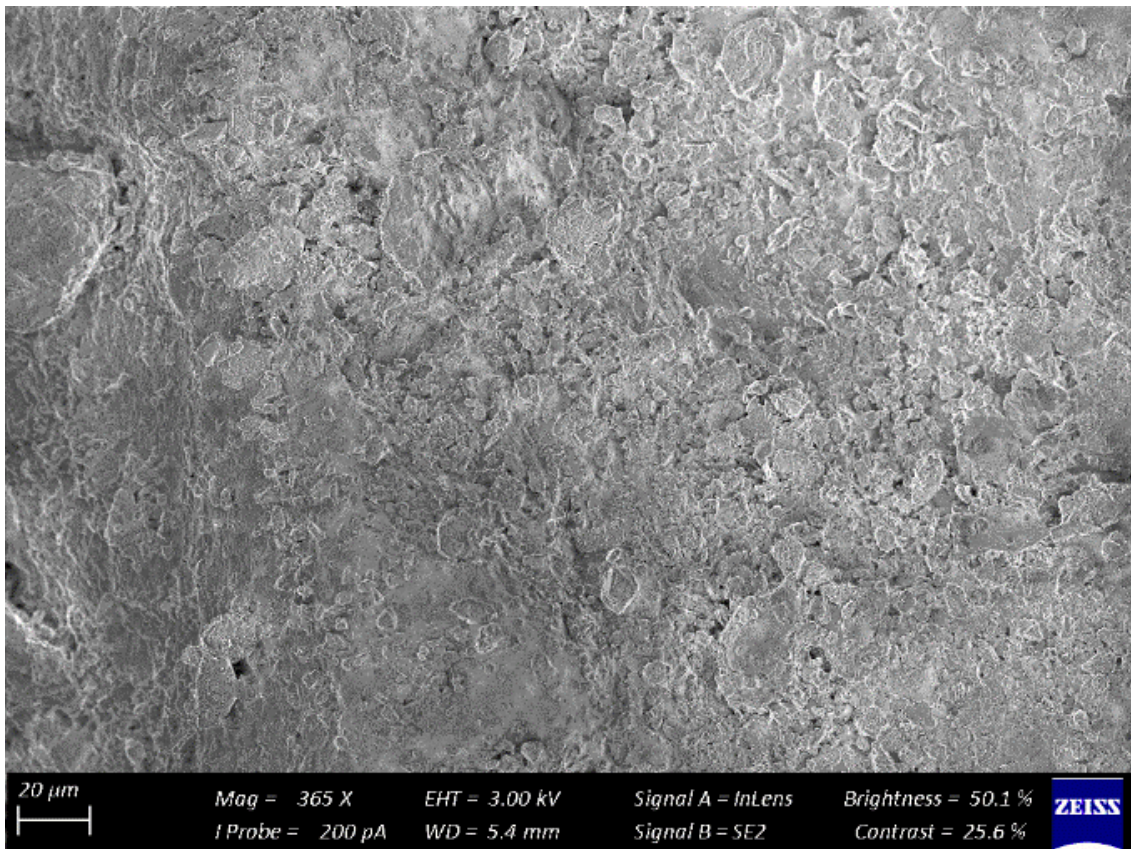




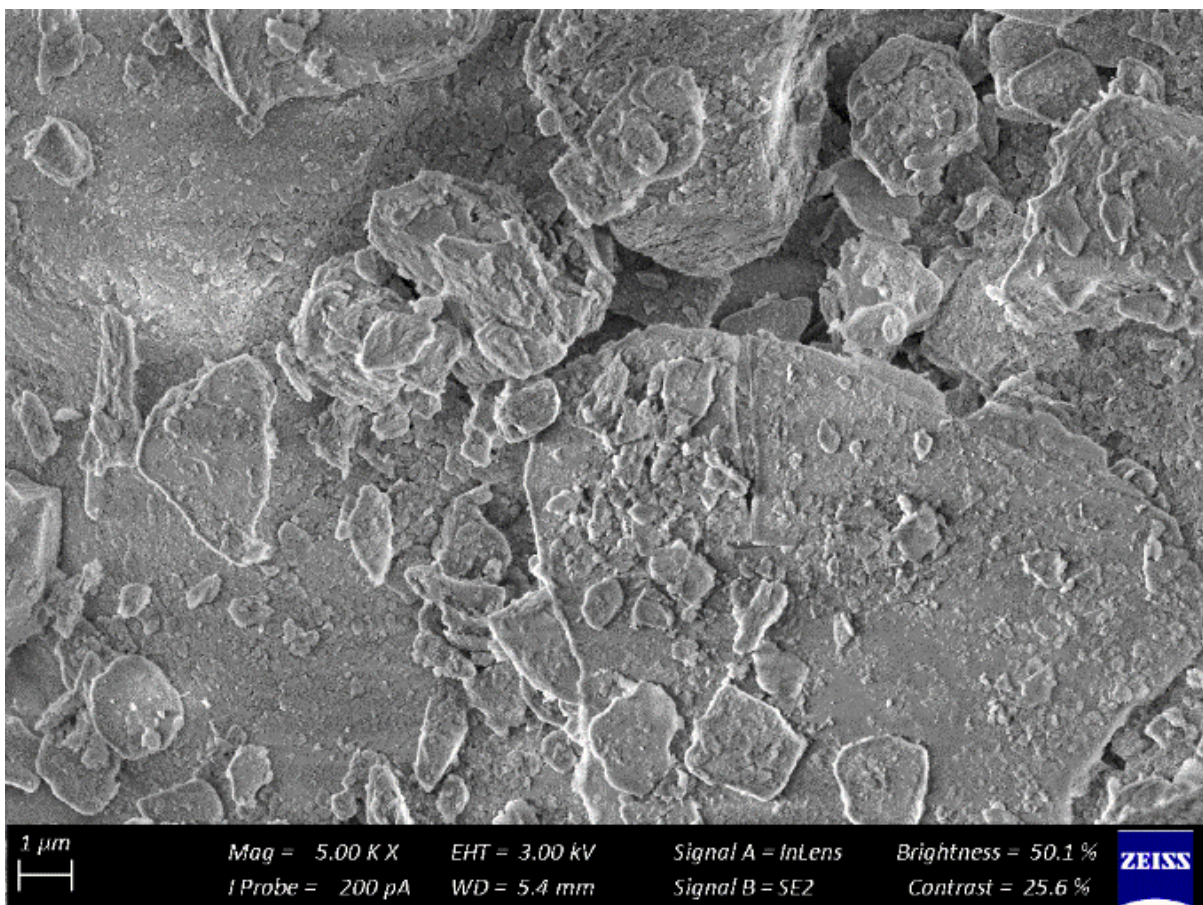
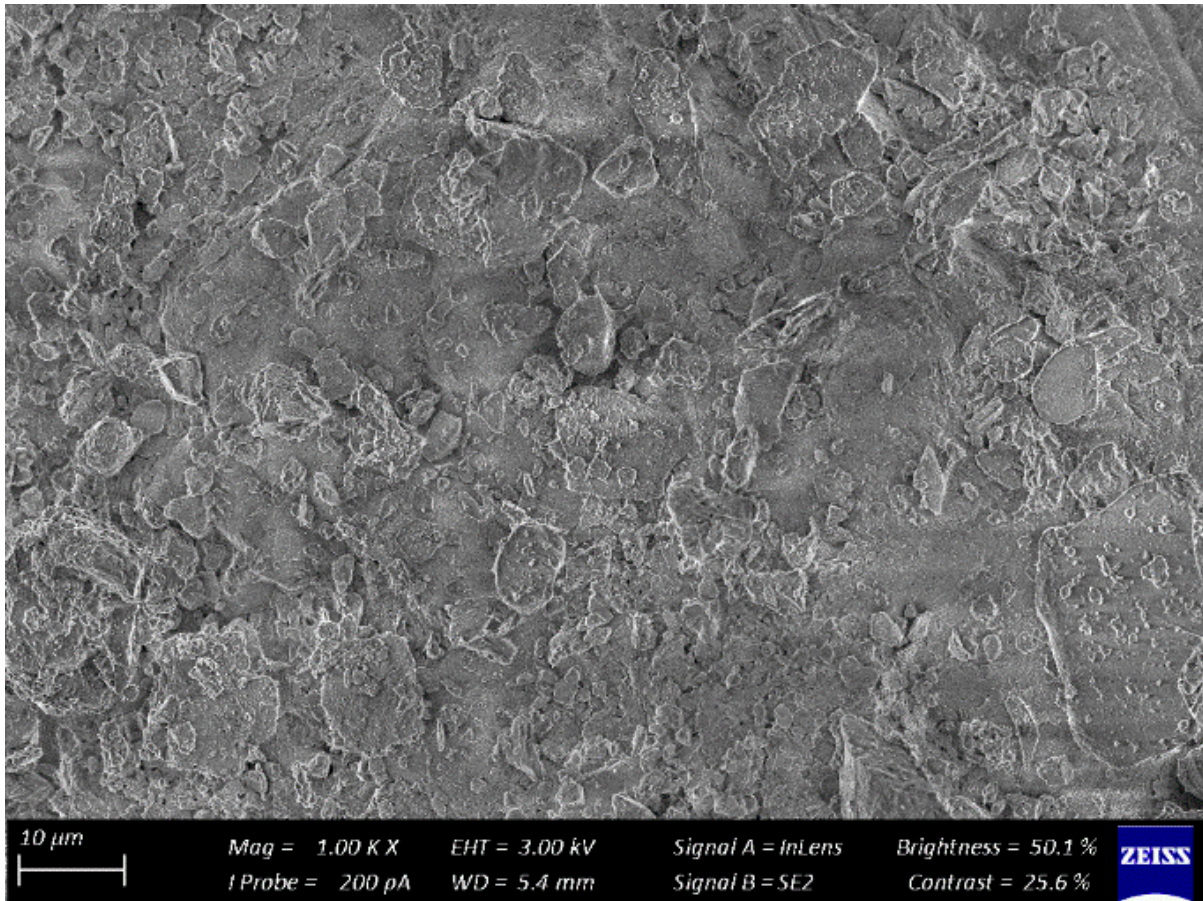




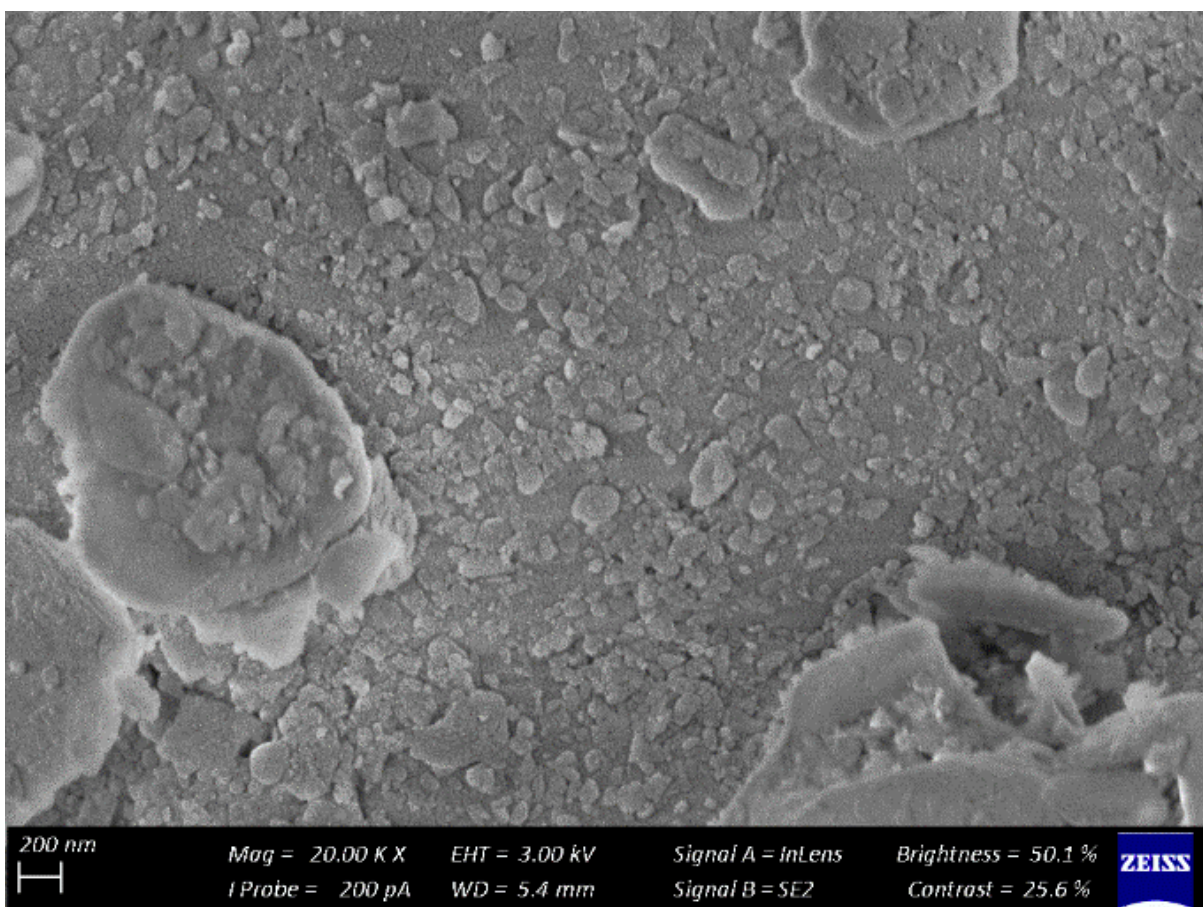
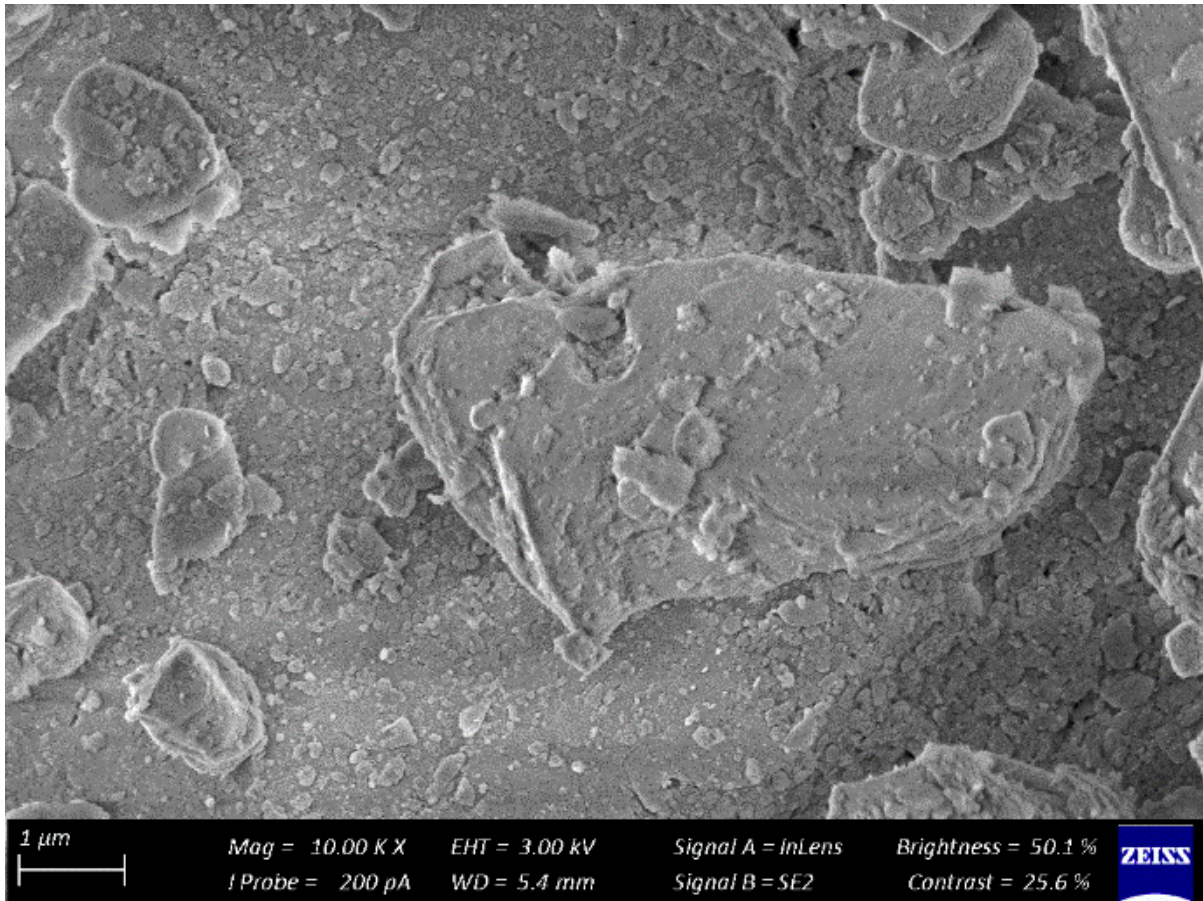
## 8.6. SEM images for Sand



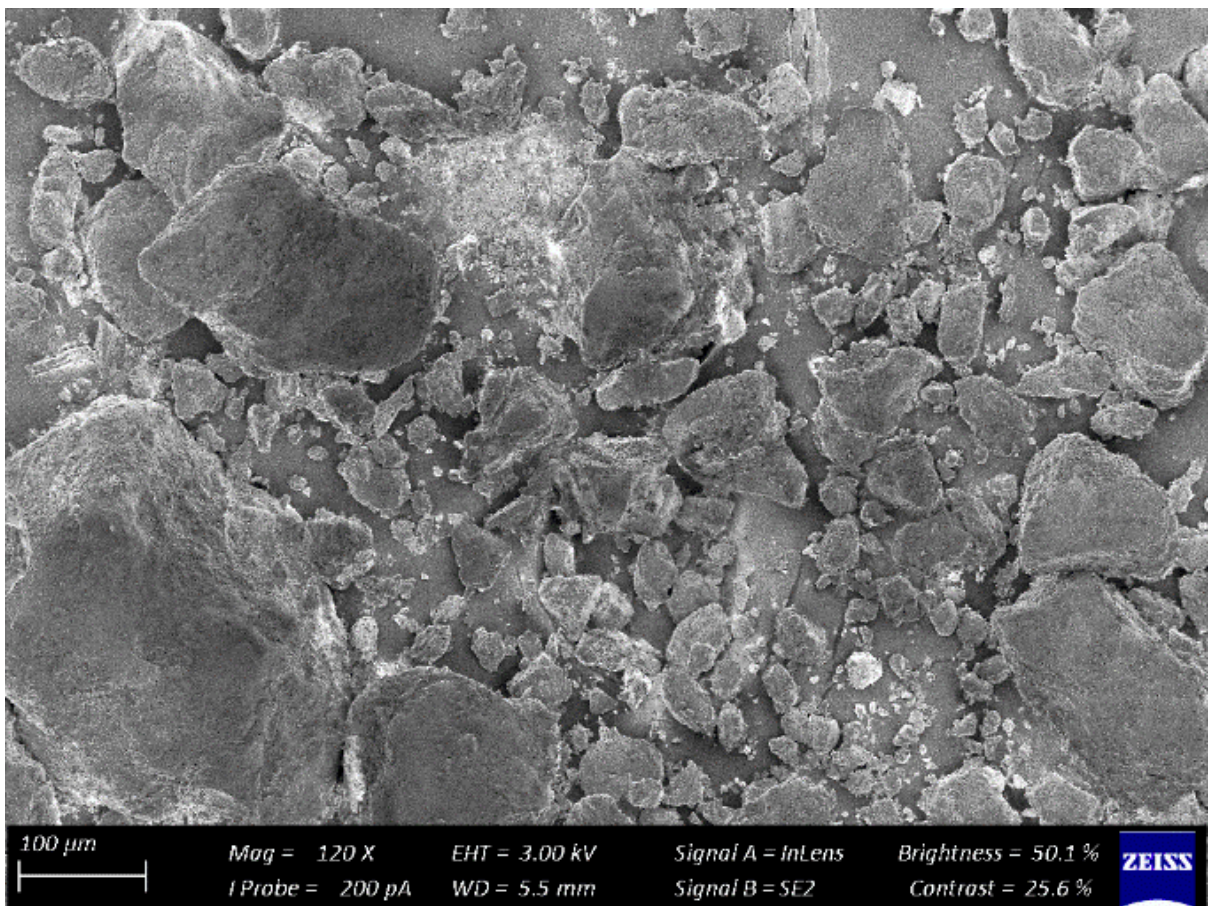
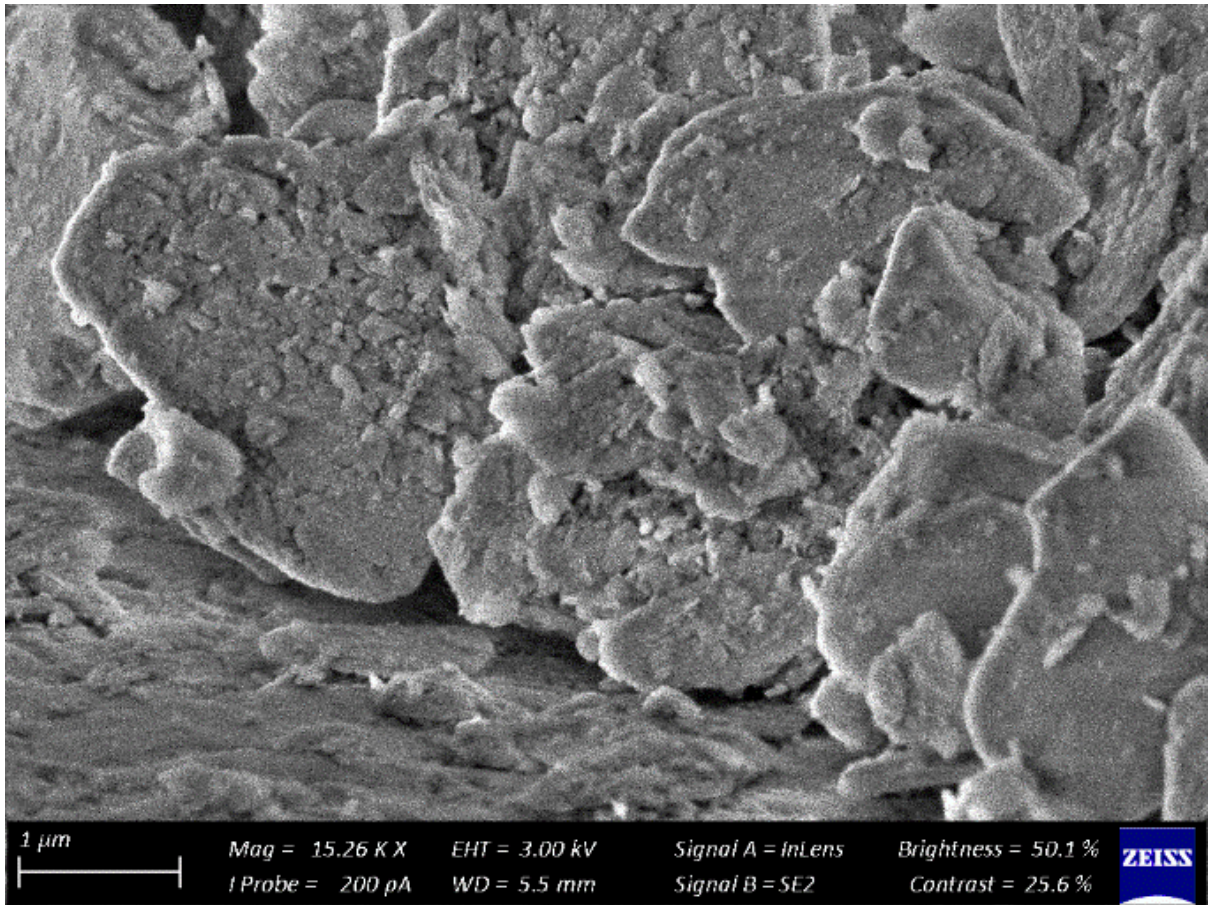




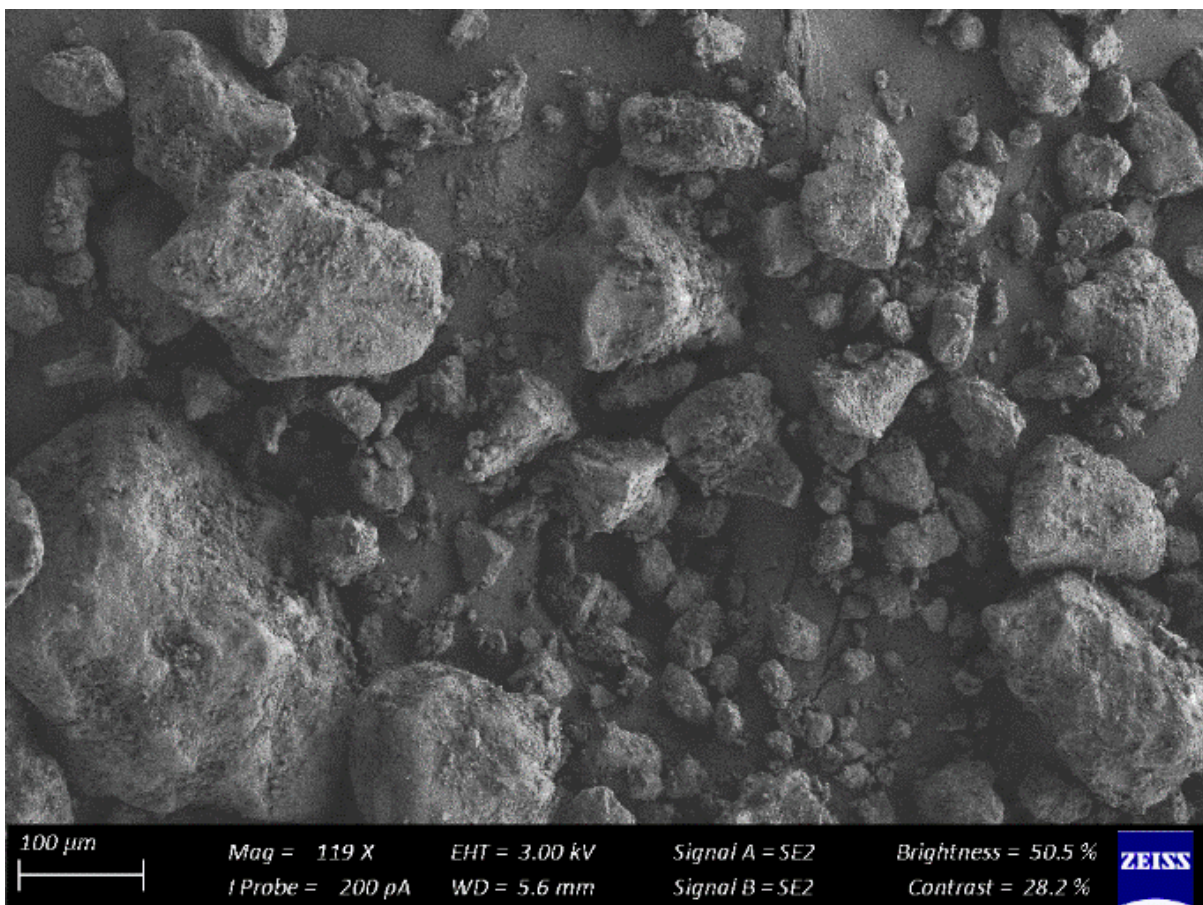
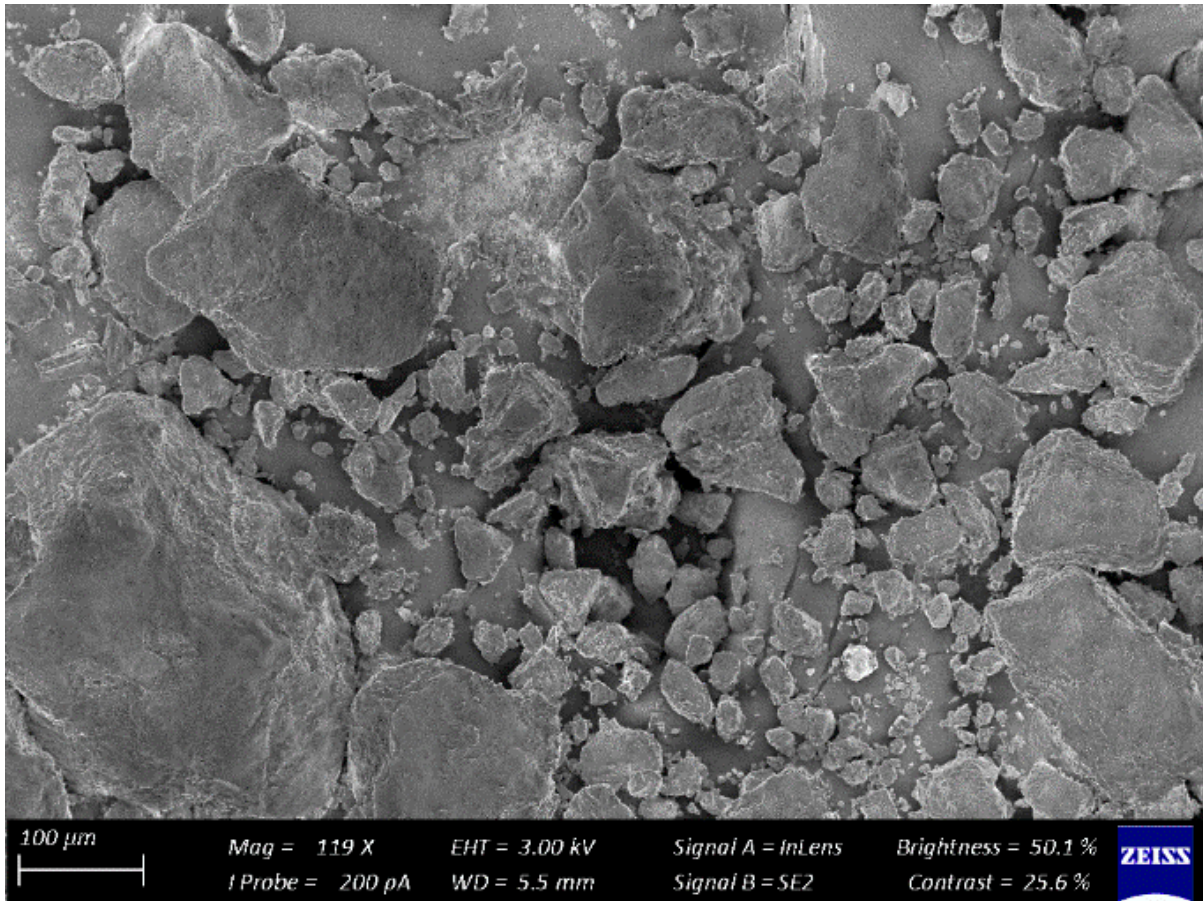








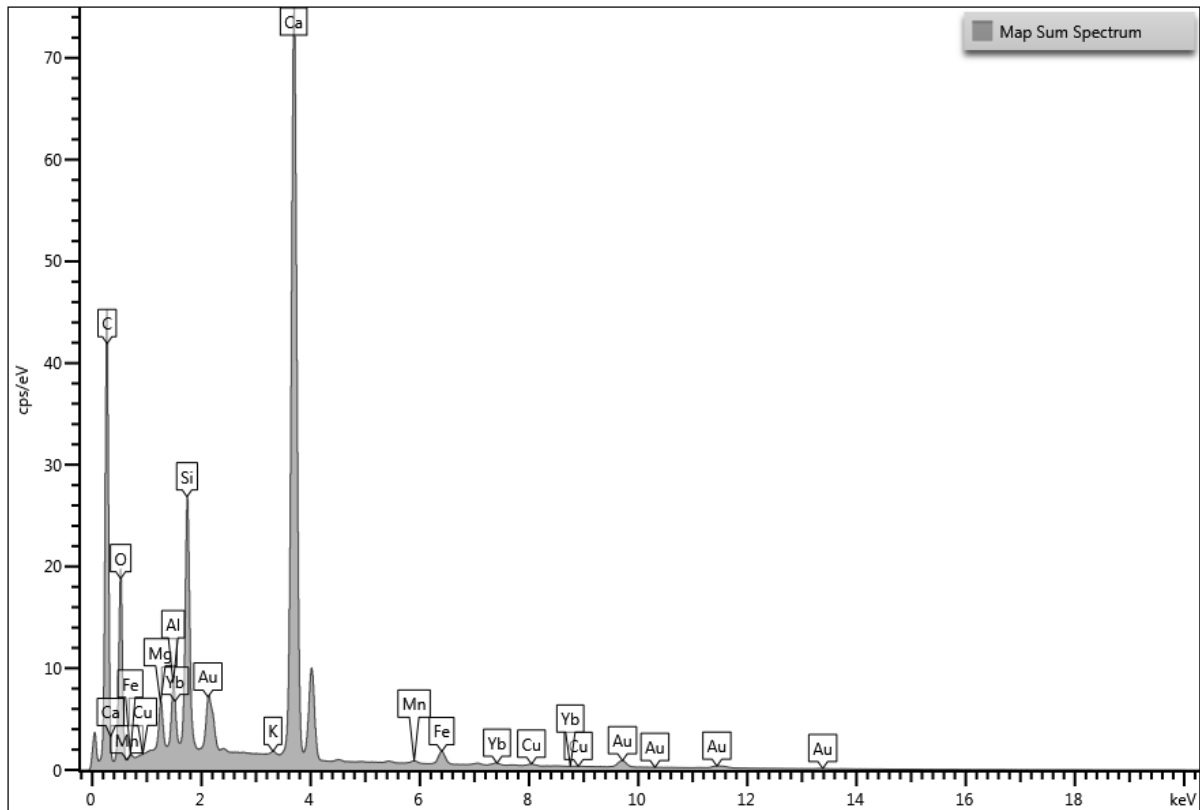
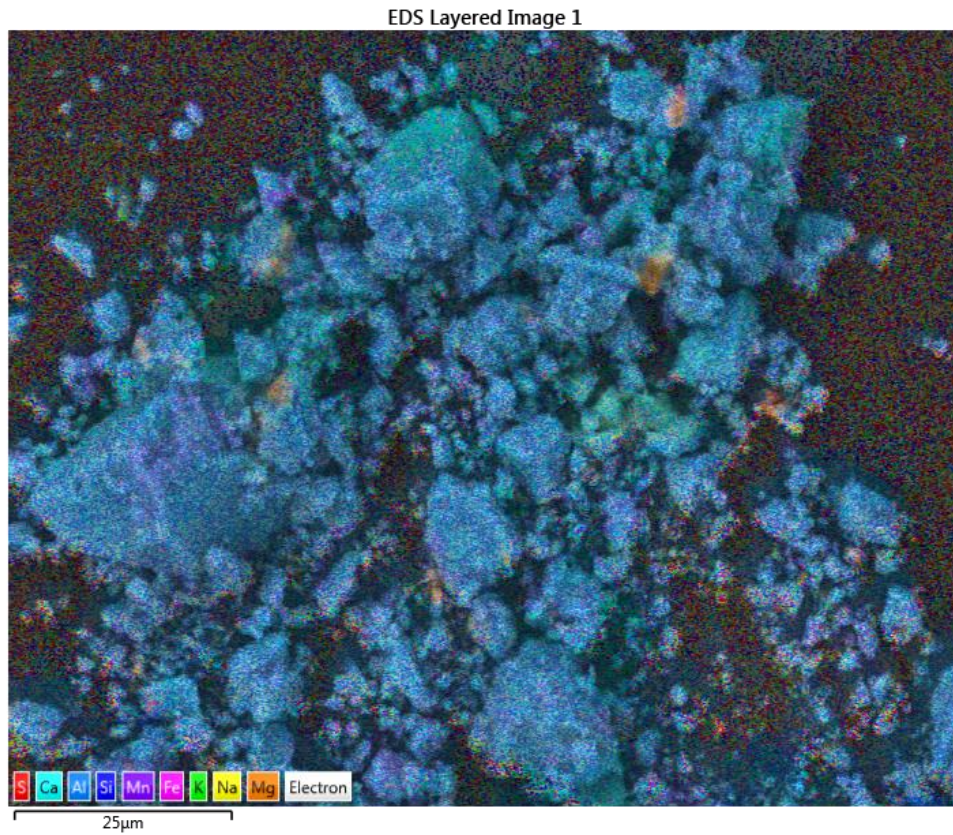






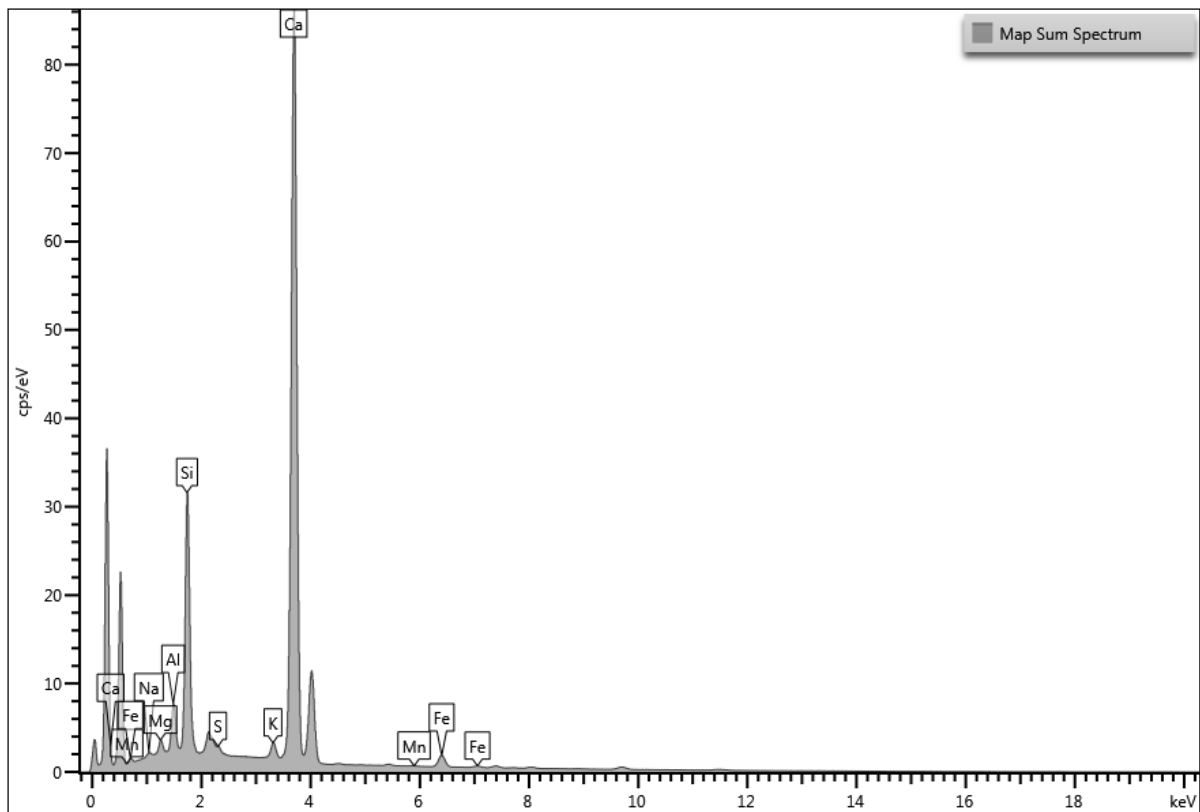
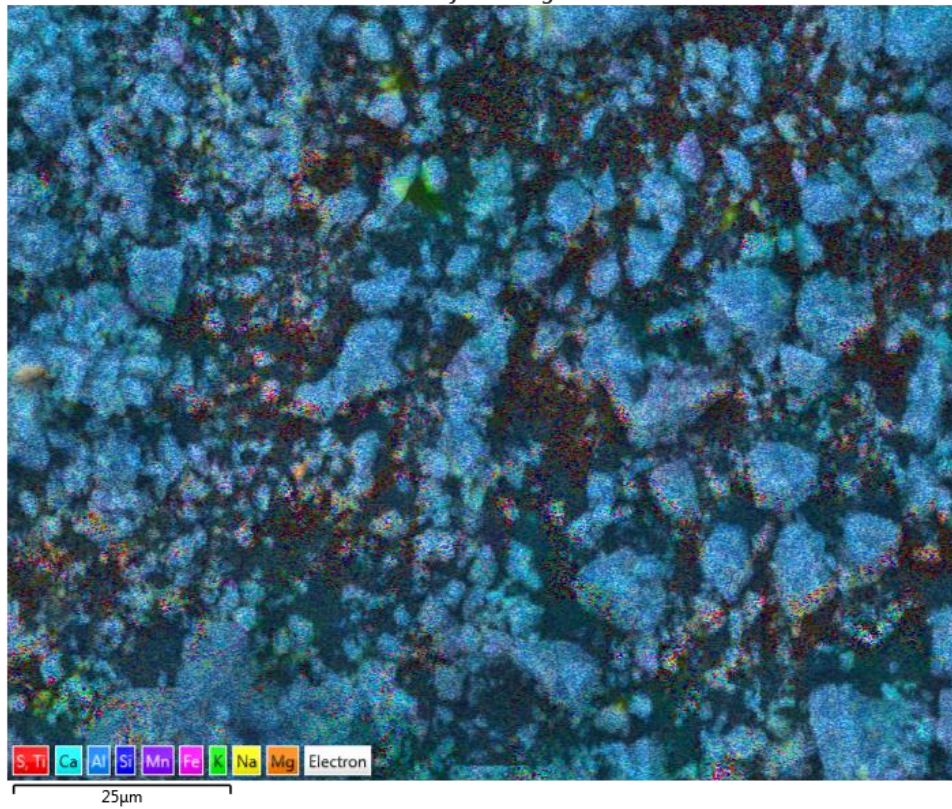
## 9. Appendix B

### 9.1. EDS result for C1 (Dwaalboom)



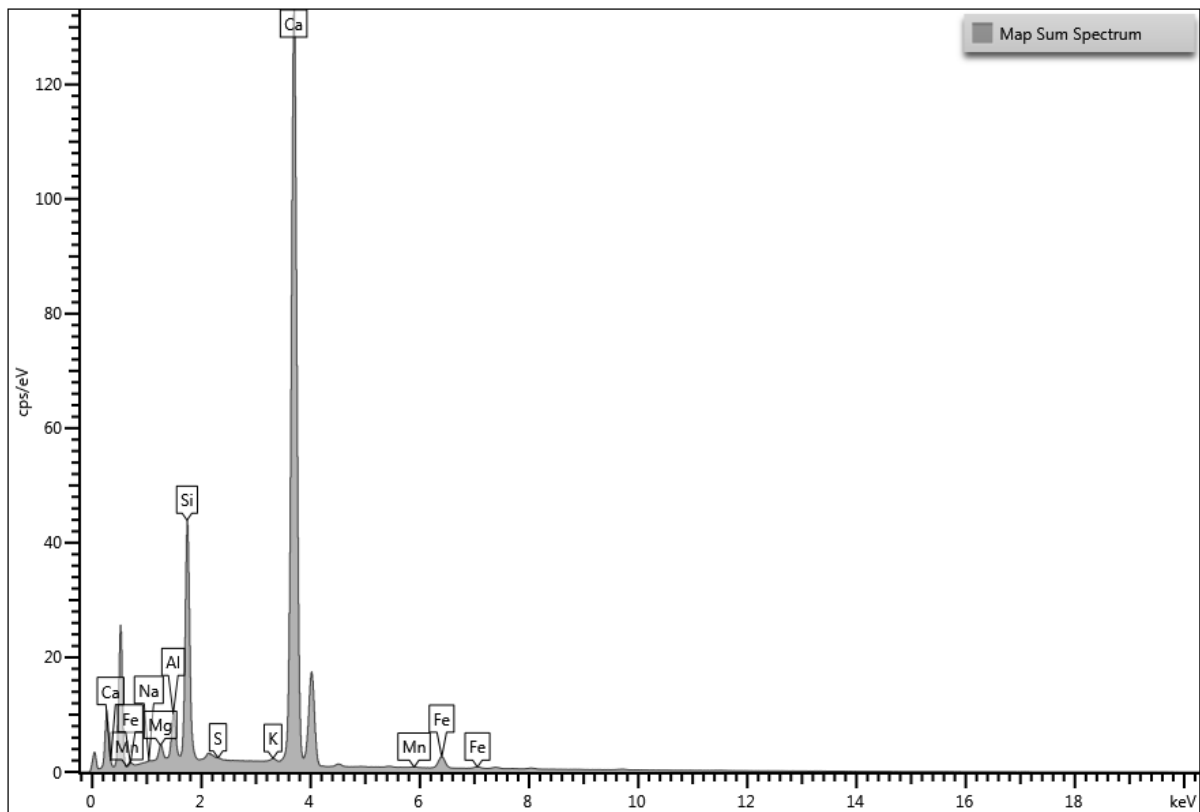
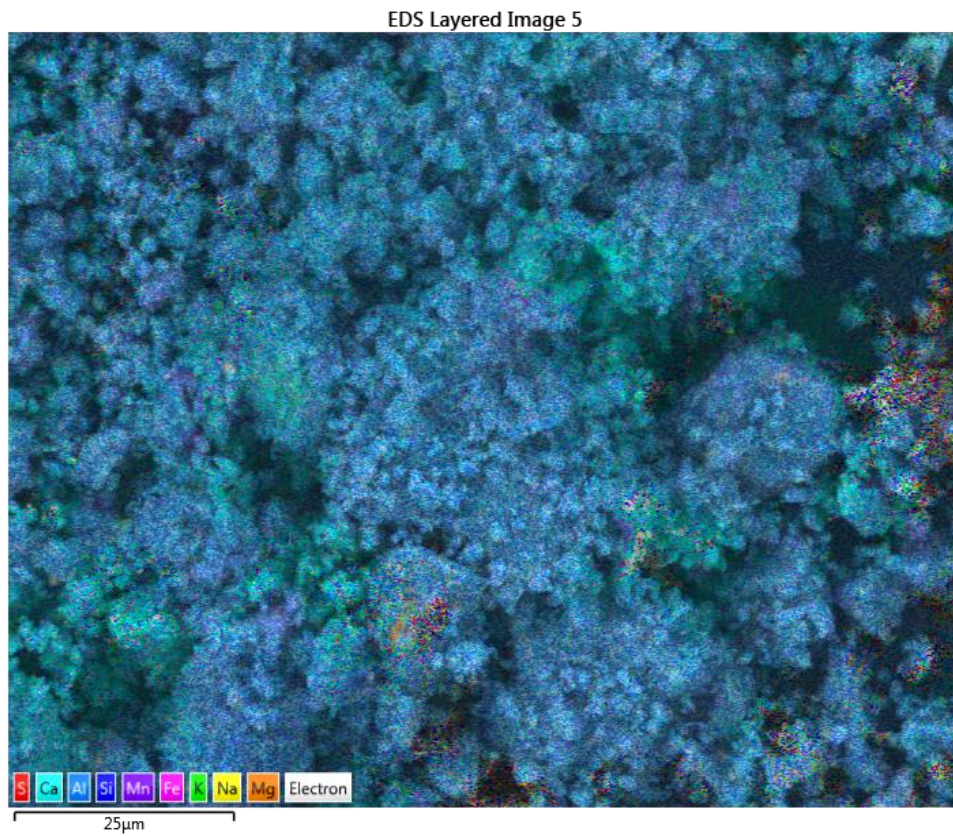
## 9.2. EDS result for C2 (De Hoek)

EDS Layered Image 4

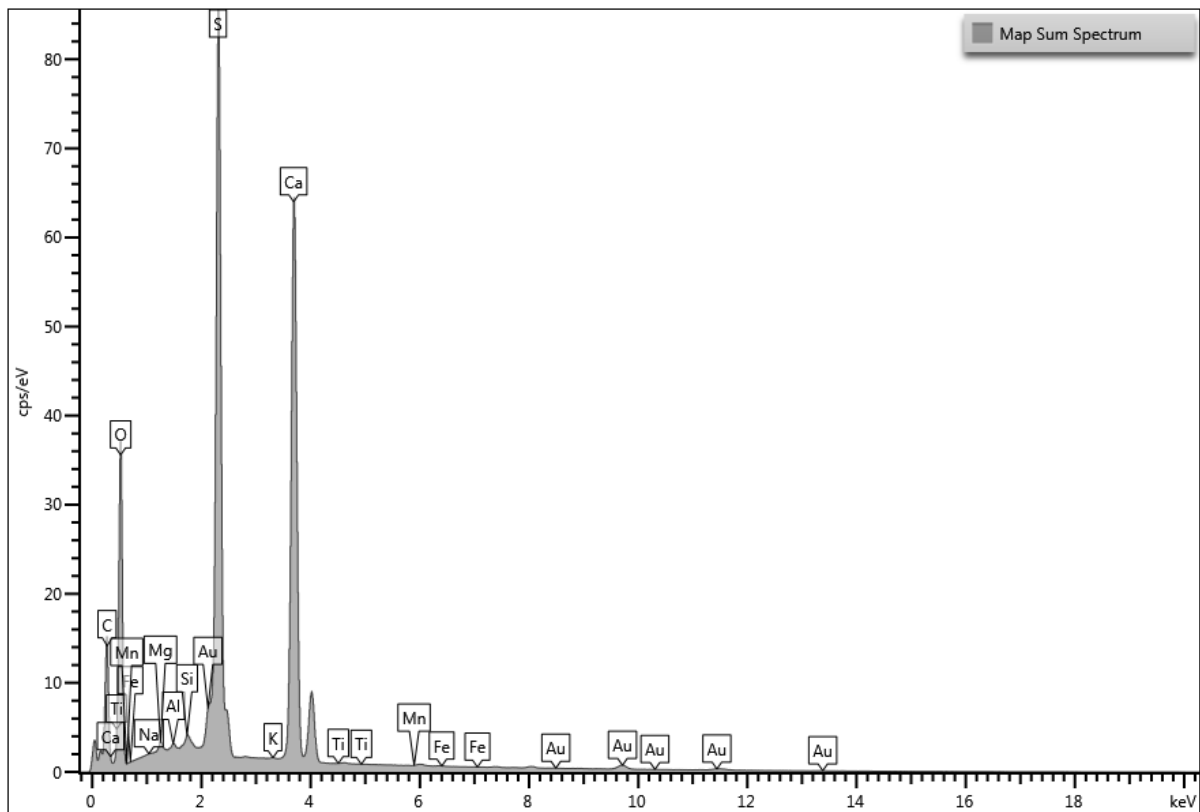




### 9.3. EDS result for C1 (Slurry)



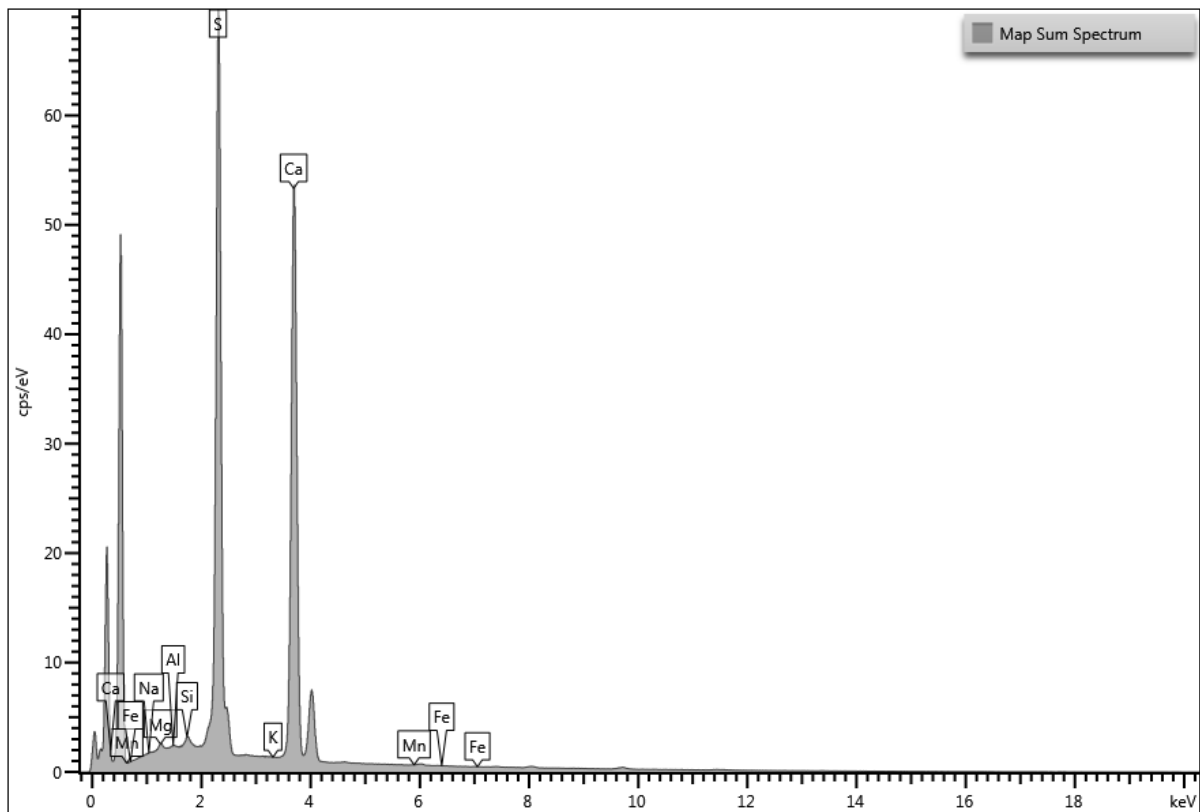
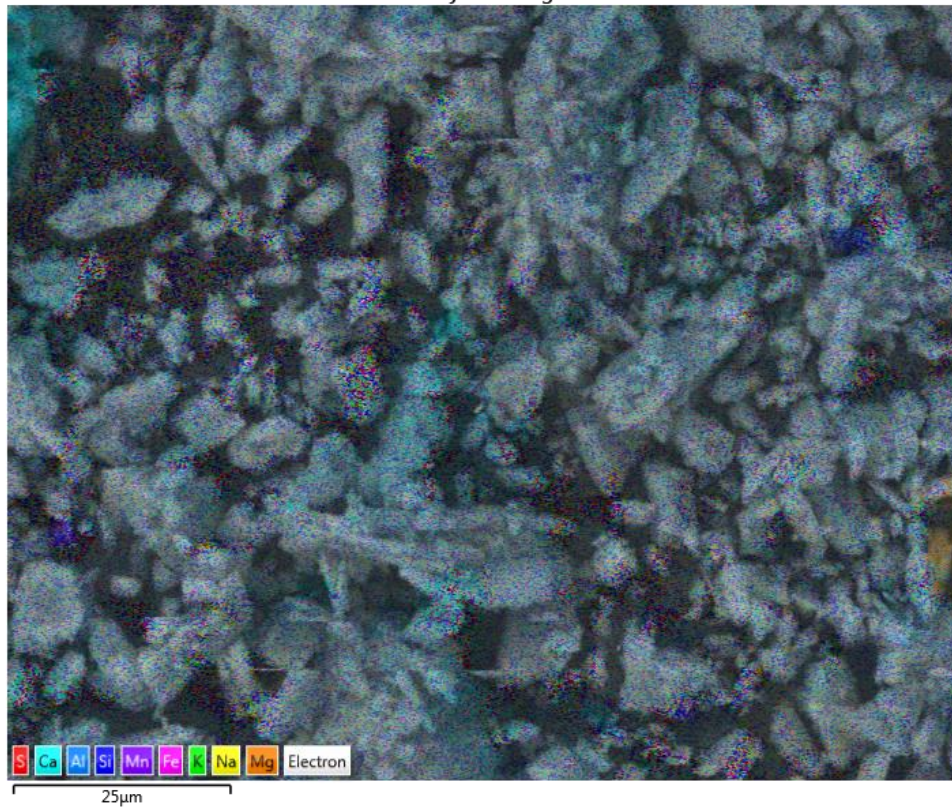
### 9.4. EDS result for G1 (Bassanite)





### 9.5. EDS result for G2 (Gypsum)

EDS Layered Image 3





## 10. Appendix C

## 10.1. Appendix C1; Particle size distribution

Particle Size	% Volume											
	Dwaalboom Clinker		Slurry Clinker		De Hoek Clinker		Bassanite		Gypsum		Sand	
[ $\mu\text{m}$ ]	Passing Sieve	Cum on Sieve	Passing Sieve	Cum on Sieve	Passing Sieve	Cum on Sieve	Passing Sieve	Cum on Sieve	Passing Sieve	Cum on Sieve	Passing Sieve	Cum on Sieve
10.000	43.45	56.55	47.92	52.08	61.22	38.78	73.33	26.67	47.16	52.84	0	100.00
16.000	3.77	52.78	0.84	51.24	9.79	28.99	8.94	17.73	14.14	38.7	0	100.00
20.000	2.39	50.39	0.16	51.08	3.77	25.22	2.61	15.12	5.71	32.99	0.02	99.98
25.000	3	47.39	0.51	50.57	3.4	21.82	1.76	13.36	5.31	27.68	0.13	99.85
32.000	3.98	43.41	1.64	48.93	3.83	17.99	1.45	11.91	5.7	21.98	0.37	99.48
38.000	3.13	40.28	1.82	47.11	2.89	15.10	1.09	10.82	3.93	18.05	0.43	99.05
45.000	3.33	36.95	2.28	44.83	3.01	12.09	1.41	9.41	3.72	14.33	0.61	98.44
53.000	3.39	33.56	2.68	42.15	2.91	9.18	1.8	7.61	3.29	11.04	0.8	97.64
63.000	3.75	29.81	3.34	38.81	2.83	6.35	2.32	5.29	3	8.04	1.11	96.53
75.000	4.05	25.76	3.89	34.92	2.36	3.99	2.44	2.85	2.49	5.55	1.44	95.09
90.000	4.59	21.17	4.64	30.28	1.81	2.18	1.98	0.87	2.08	3.47	1.87	93.22
106.000	4.38	16.79	4.71	25.57	1.08	1.10	0.77	0.10	1.47	2.00	2.04	91.18

125.00 0	4.45	12.3 4	5.32	20.2 5	0.66	0.44	0.1	0.00	1.1	0.90	2.41	88.77
150.00 0	4.51	7.83	6.28	13.9 7	0.31	0.13	0	0.00	0.74	0.16	3.13	85.64
180.00 0	3.6	4.23	5.99	7.98	0.11	0.02	0	0.00	0.16	0.00	3.7	81.94
212.00 0	2.26	1.97	4.33	3.65	0.02	0.00	0	0.00	0	0.00	3.93	78.01
250.00 0	1.36	0.61	2.81	0.84	0	0.00	0	0.00	0	0.00	4.72	73.29
300.00 0	0.53	0.08	0.84	0.00	0	0.00	0	0.00	0	0.00	6.32	66.97

10.2. Appendix C2; Gypsum addition formula

# Memorandum

**From:** Frans Scheurwater  
**To:** Petrus  
**Date:** 12 April 2018  
**Reference:** Saint Gobain - Gypsum Waste Products

## Saint Gobain - Fine waste

SO <sub>3</sub> of Gypsum	43.32 %	% Gypsum =	$\frac{\text{SO}_3 \text{ of cement} - \text{SO}_3 \text{ of Clinker} \times 100}{\text{SO}_3 \text{ of Gypsum} - \text{SO}_3 \text{ of Clinker}}$
Clinker SO <sub>3</sub> content	1.10 %		
For Target SO <sub>3</sub> content of	2.34 %	% Gypsum =	$\frac{2.3 - 1.1 \times 100}{43.32 - 1.1}$
		% Gypsum =	2.937
Clinker:	De Hoek 1577371	97.06 %	3882.5 g
Gypsum:	1812021 Saint Gobain - Fine	2.94 %	117.5 g
Cement No.:	1826076		4000.0 g

<b>SURFACE AREA AIM =</b>	<b>4000 cm<sup>2</sup>/g</b>	<b>RD=</b>	
Grind	Revs + 600	Surface Area =	_____ cm <sup>2</sup> /g
	Revs + 500	Surface Area =	_____ cm <sup>2</sup> /g
	Revs + 500	Surface Area =	_____ cm <sup>2</sup> /g
	Revs + 800	Surface Area =	_____ cm <sup>2</sup> /g
	Revs + 1000	Surface Area =	_____ cm <sup>2</sup> /g
	Revs + 300	Surface Area =	_____ cm <sup>2</sup> /g
	Revs +	Surface Area =	_____ cm <sup>2</sup> /g
Homoginised		Surface Area =	_____ cm <sup>2</sup> /g

## Saint Gobain -Gypsum Board Waste

SO <sub>3</sub> of Gypsum	38.50 %	% Gypsum =	$\frac{\text{SO}_3 \text{ of cement} - \text{SO}_3 \text{ of Clinker} \times 100}{\text{SO}_3 \text{ of Gypsum} - \text{SO}_3 \text{ of Clinker}}$
Clinker SO <sub>3</sub> content	0.19 %		
For Target SO <sub>3</sub> content of	2.34 %	% Gypsum =	$\frac{2.3 - 0.19 \times 100}{38.5 - 0.19}$
		% Gypsum =	5.612
Clinker:	H Ali trial 1577371	94.39 %	3681.1 g
Gypsum:	1812020 Saint Gobain -Gyps	5.61 %	218.9 g
Cement No.:	1826079		3900.0 g

<b>SURFACE AREA AIM =</b>	<b>4000 cm<sup>2</sup>/g</b>	<b>RD=</b>	
Grind	Revs + 200	Surface Area =	_____ cm <sup>2</sup> /g
	Revs + 200	Surface Area =	_____ cm <sup>2</sup> /g
	Revs + 200	Surface Area =	_____ cm <sup>2</sup> /g
	Revs +	Surface Area =	_____ cm <sup>2</sup> /g
	Revs +	Surface Area =	_____ cm <sup>2</sup> /g
	Revs +	Surface Area =	_____ cm <sup>2</sup> /g
	Revs +	Surface Area =	_____ cm <sup>2</sup> /g
Homoginised		Surface Area =	_____ cm <sup>2</sup> /g

Notes: \_\_\_\_\_

## 11. Appendix D

## 11.1. Appendix D1; Mini slump results

Code	Mix Description	Setting time [seconds]			
		T0	T20	T40	T60
DW1	Clnk1 (reference)	67.5	67.72	66.83	64.33
DW2	Clnk1 + 0.2% SP1	81	84.75	77.75	74
DW3	Clnk1 + 0.5% SP1	100.25	100.75	97	92.5
DW4	Clnk1 + 0.9% SP1	132.5	124.75	120.5	114.75
DW5	Clnk1 + 0.2% SP2	82	80.75	78.75	76.25
DW6	Clnk1 + 0.5% SP2	91.75	89.75	83.75	80.25
DW7	Clnk1 + 0.9% SP2	125.5	123.25	113.5	107.75
DW8	Clnk1 + 0.2% SP3	80.75	82	77.5	69.25
DW9	Clnk1 + 0.5% SP3	89.25	88.5	83.5	80.75
DW10	Clnk1 + 0.9% SP3	108.5	104.75	99.75	98.75
DW11	Clnk1 + 0.2% SP4	59.5	58.75	53.75	55.25
DW12	Clnk1 + 0.5% SP4	57.5	56.25	50.75	54.5
DW13	Clnk1 + 0.9% SP4	59.25	56	56.75	54.5
DW14	Clnk1 + 2% G1	56.25	40	40	40
DW15	Clnk1 + 4% G1	55.5	49	40	40
DW16	Clnk1 + 6% G1	52	44.75	43	40
DW17	Clnk1 + 0.2% SP1 + 2% G1	76.5	40	40	40
DW18	Clnk1 + 0.9% SP1 + 2% G1	138	118.75	109.25	101.5
DW19	Clnk1 + 0.2% SP2 + 2% G1	69.75	67.5	61.5	52.25
DW20	Clnk1 + 0.9% SP2 + 2% G1	144.25	102.75	95.5	91.5
DW21	Clnk1 + 0.2% SP3 + 2% G1	70	40	40	40
DW22	Clnk1 + 0.9% SP3 + 2% G1	142.5	88.5	83	78
DW23	Clnk1 + 0.2% SP4 + 2% G1	51	40	40	40
DW24	Clnk1 + 0.9% SP4 + 2% G1	68.25	40	40	40
DW25	Clnk1 + 0.2% SP1 + 6% G1	73	59.25	50	42.25
DW26	Clnk1 + 0.9% SP1 + 6% G1	147.5	147.75	148.5	143
DW27	Clnk1 + 0.2% SP2 + 6% G1	70	66.5	54.25	47.25
DW28	Clnk1 + 0.9% SP2 + 6% G1	119.25	126.25	133	132.5
DW29	Clnk1 + 0.2% SP3 + 6% G1	81	78.5	71.5	65.25
DW30	Clnk1 + 0.9% SP3 + 6% G1	121.25	125.25	130.75	131
DW31	Clnk1 + 0.2% SP4 + 6% G1	59.5	52.25	43.75	40
DW32	Clnk1 + 0.9% SP4 + 6% G1	69.25	64	51.5	42.25
DW35	Clnk1 + 2% G2	47.25	40	40	40
DW36	Clnk1 + 6% G2	46.5	43.25	41.25	40
DW37	Clnk1 + 0.9% SP1 + 6% G2	136.5	136.5	133.25	122.75
DW38	Clnk1 + 0.9% SP2 + 6% G2	134.75	129.75	128.5	122.5
DW39	Clnk1 + 0.9% SP3 + 6% G2	135.5	131.75	127.5	119
DW40	Clnk1 + 0.9% SP4 + 6% G2	74.5	51.25	43.5	40.5

Code	Mix Description	T0	T20	T40	T60
DH1	Clnk2 (reference)	59.58	41.33	40.33	40
DH2	Clnk2 + 0.2% SP1	77.75	47.25	46.25	40.25
DH3	Clnk2 + 0.5% SP1	135	96.25	78	78.5
DH4	Clnk2 + 0.9% SP1	144.25	138.75	108.75	108.5
DH5	Clnk2 + 0.2% SP2	83.75	56	47	41.5
DH6	Clnk2 + 0.5% SP2	127.25	82.25	69.25	61
DH7	Clnk2 + 0.9% SP2	146.25	141.25	116.75	108.25
DH8	Clnk2 + 0.2% SP3	90.75	55.75	54.75	52.5
DH9	Clnk2 + 0.5% SP3	119.5	79.25	66.25	65
DH10	Clnk2 + 0.9% SP3	140.5	117	92	85.25
DH11	Clnk2 + 0.2% SP4	69	40	40	40
DH12	Clnk2 + 0.5% SP4	82.75	61.75	49	40.5
DH13	Clnk2 + 0.9% SP4	107	83.5	74.75	67.25
DH14	Clnk2 + 2% G1	61	59	55.5	47.25
DH15	Clnk2 + 4% G1	60.25	58.5	50.5	41
DH16	Clnk2 + 6% G1	55	52.5	44.25	40
DH17	Clnk2 + 0.2% SP1 + 2% G1	88.5	74.75	69	58.75
DH18	Clnk2 + 0.9% SP1 + 2% G1	145	141.75	143.75	143.5
DH19	Clnk2 + 0.2% SP2 + 2% G1	75	54	62	53.25
DH20	Clnk2 + 0.9% SP2 + 2% G1	129.25	133.75	138.75	138.25
DH21	Clnk2 + 0.2% SP3 + 2% G1	77.5	75.75	70.25	65.5
DH22	Clnk2 + 0.9% SP3 + 2% G1	123.5	119.75	120.25	120
DH23	Clnk2 + 0.2% SP4 + 2% G1	65	47.25	51.5	43.75
DH24	Clnk2 + 0.9% SP4 + 2% G1	78	69.75	62	53.75
DH25	Clnk2 + 0.2% SP1 + 6% G1	84.75	65.75	55.5	45.25
DH26	Clnk2 + 0.9% SP1 + 6% G1	140	141.5	140.5	144.5
DH27	Clnk2 + 0.2% SP2 + 6% G1	73.5	61.5	50	42
DH28	Clnk2 + 0.9% SP2 + 6% G1	108.5	121.25	127	127.75
DH29	Clnk2 + 0.2% SP3 + 6% G1	71.25	67	60.75	49.75
DH30	Clnk2 + 0.9% SP3 + 6% G1	88.25	105.5	113.5	110
DH31	Clnk2 + 0.2% SP4 + 6% G1	53.5	45.75	41.75	40
DH32	Clnk2 + 0.9% SP4 + 6% G1	65.75	54.25	47	40
DH35	Clnk2 + 2% G2	68	56	50	46
DH36	Clnk2 + 6% G2	63.75	56.25	48.5	44.75
DH37	Clnk2 + 0.9% SP1 + 6% G2	141	142.25	145.25	142.5
DH38	Clnk2 + 0.9% SP2 + 6% G2	135.25	138	138.75	139.25
DH39	Clnk2 + 0.9% SP3 + 6% G2	134.25	127	121.75	118.5
DH40	Clnk2 + 0.9% SP4 + 6% G2	97.25	84.75	77	72



Code	Mix Description	T0	T20	T40	T60
SL1	Clnk3 (reference)	51	49.67	42.33	40
SL2	Clnk3 + 0.2% SP1	73.25	68.5	64	58
SL3	Clnk3 + 0.5% SP1	87	83.25	77.5	74.25
SL4	Clnk3 + 0.9% SP1	118	106	96	92
SL5	Clnk3 + 0.2% SP2	72.75	66.75	62.75	54.5
SL6	Clnk3 + 0.5% SP2	88.25	80.5	76	71.5
SL7	Clnk3 + 0.9% SP2	128	117.25	107.5	100.75
SL8	Clnk3 + 0.2% SP3	75.5	68.75	64.75	56.75
SL9	Clnk3 + 0.5% SP3	84.25	79	75.5	70.25
SL10	Clnk3 + 0.9% SP3	100.5	97.25	89.75	86.5
SL11	Clnk3 + 0.2% SP4	53.5	47.5	47.25	40
SL12	Clnk3 + 0.5% SP4	54.25	50.25	47.75	42.25
SL13	Clnk3 + 0.9% SP4	64	63.75	50.75	44.5
SL14	Clnk3 + 2% G1	65.5	51.75	42.75	40
SL15	Clnk3 + 4% G1	53.25	45.5	40	40
SL16	Clnk3 + 6% G1	57	44	40	40
SL17	Clnk3 + 0.2% SP1 + 2% G1	72.75	56	45.25	40.5
SL18	Clnk3 + 0.9% SP1 + 2% G1	131	137.25	137.75	117.25
SL19	Clnk3 + 0.2% SP2 + 2% G1	75.25	66	55.5	44
SL20	Clnk3 + 0.9% SP2 + 2% G1	133.75	133.75	139	138.75
SL21	Clnk3 + 0.2% SP3 + 2% G1	77.25	71.75	61.5	50.5
SL22	Clnk3 + 0.9% SP3 + 2% G1	134.5	132.5	132.75	122.75
SL23	Clnk3 + 0.2% SP4 + 2% G1	60	49.25	44.75	40.25
SL24	Clnk3 + 0.9% SP4 + 2% G1	77.5	63	47.75	41.75
SL25	Clnk3 + 0.2% SP1 + 6% G1	65.75	48	41.25	40
SL26	Clnk3 + 0.9% SP1 + 6% G1	135.75	132.75	136	134
SL27	Clnk3 + 0.2% SP2 + 6% G1	59.25	60.25	43.75	40
SL28	Clnk3 + 0.9% SP2 + 6% G1	112.75	127.25	130.75	127.75
SL29	Clnk3 + 0.2% SP3 + 6% G1	75.5	72.5	60.75	45.25
SL30	Clnk3 + 0.9% SP3 + 6% G1	121.25	122	125.25	129.25
SL31	Clnk3 + 0.2% SP4 + 6% G1	46.5	41.75	40	40
SL32	Clnk3 + 0.9% SP4 + 6% G1	69.75	62.25	45.25	40
SL35	Clnk3 + 2% G2	57.25	45.75	40.75	40
SL36	Clnk3 + 6% G2	59	46.25	42.25	40
SL37	Clnk3 + 0.9% SP1 + 6% G2	136.25	135.25	133.5	126.5
SL38	Clnk3 + 0.9% SP2 + 6% G2	131	132	133.25	129.5
SL39	Clnk3 + 0.9% SP3 + 6% G2	129.25	132.75	133.75	131.5
SL40	Clnk3 + 0.9% SP4 + 6% G2	85.75	76.25	68.25	60.25

## 11.2. Appendix D2; Marsh cone results

		Marsh cone results [seconds]							
		T0	Test Description	T20	Test Description	T40	Test Description	T60	Test Description
DW1	Clinker1 (reference)	40.03		34.9		37.27	2% remain	40.24	8% remain
DW2	Clinker1 + 0.2% SP1	29.4		25.61		27.63		31.5	
DW3	Clinker1 + 0.5% SP1	22.55		19.6		19.36		19.21	
DW4	Clinker1 + 0.9% SP1	18.53		18.16		18.23		18.06	
DW5	Clinker1 + 0.2% SP2	29.29		24.69		25.61		27.52	
DW6	Clinker1 + 0.5% SP2	26.49		25.07		26.42		29.32	
DW7	Clinker1 + 0.9% SP2	20.55		19.09		19.8		19.44	
DW8	Clinker1 + 0.2% SP3	31.47		28.6		32.04		42.4	
DW9	Clinker1 + 0.5% SP3	24.1		22.92		24.36		26.23	
DW10	Clinker1 + 0.9% SP3	18.52		16.2		16.3		16.5	
DW11	Clinker1 + 0.2% SP4	27.07	flow stop - 50% remain	14.53	flow stop - 80% remain	5.52	flow stop - 85% remain	2.89	flow stop 90% remain
DW12	Clinker1 + 0.5% SP4	9.36	80% remain	5.55	80% remain	4.42	95% remain	3.92	97% remain
DW13	Clinker1 + 0.9% SP4	32.32	50% remain	14.49	75% remain	7.8	96% remain	3.86	98% remain
DW14	Clinker1 + 2% G1	42.81	50% remain		false set		false set		false set
DW15	Clinker1 + 4% G1	37.27	50% remain	3.92	94% remain		few drops		no drops
DW16	Clinker1 + 6% G1	22.86	73% remain	3.25	95% remain		few drops		no drops
DW17	Clinker1 + 0.2 SP1 + 2% G1	47.83			false set		false set		false set
DW18	Clinker1 + 0.9% SP1 + 2% G1	15.93	segregate	22.7		22.47		23.36	
DW19	Clinker1 + 0.2 SP2 + 2% G1	35.92	false set if left for few minutes	57.46		50.09	27% remain	8.18	86% remain
DW20	Clinker1 + 0.9% SP2 + 2% G1	16.04	segregate	28.36		27.55		27.4	
DW21	Clinker1 + 0.2 SP3 + 2% G1	34.09			false set		false set		false set
DW22	Clinker1 + 0.9% SP3 + 2% G1	15.23	segregate	29.8		28.12		28.84	
DW23	Clinker1 + 0.2 SP4 + 2% G1	8.52	82% remain		false set		false set		false set
DW24	Clinker1 + 0.9% SP4 + 2% G1	43.8	false set if left for few minutes		no drops		no drops		no drops
DW25	Clinker1 + 0.2 SP1 + 6% G1	44.56	4% remain	39.56	40% remain	2.15	97% remain		few drops
DW26	Clinker1 + 0.9% SP1 + 6% G1	15.76	segregate	15.35	segregate	15.49	segregate	15.53	segregate
DW27	Clinker1 + 0.2 SP2 + 6% G1	42.76		39.43		33.35	45% remain	1.69	98% remain
DW28	Clinker1 + 0.9% SP2 + 6% G1	16.15		14.89		15.06		15.49	
DW29	Clinker1 + 0.2 SP3 + 6% G1	21.6		21.96		30		41.03	3% remain
DW30	Clinker1 + 0.9% SP3 + 6% G1	14.84		14.27		14.13		14.32	
DW31	Clinker1 + 0.2 SP4 + 6% G1	41.95	30% remain	4.95	80% remain	0.83	95% remain		few drops
DW32	Clinker1 + 0.9% SP4 + 6% G1	33.47		37.92	7% remain	4.01	85% remain	0.96	97% remain
DW35	Clinker1 + 2% G2	2.8	95% remain		false set		false set		false set
DW36	Clinker1 + 6% G2	4.36	86% remain	0.89	98% remain		few drops		no drops
DW37	Clinker1 + 0.9% SP1 + 6% G2	14.69	segregate	14.52	segregate	13.84		14.8	
DW38	Clinker1 + 0.9% SP2 + 6% G2	14.44		14.35		14.35		14.72	
DW39	Clinker1 + 0.9% SP3 + 6% G2	13.89		13.7		13.91		13.82	
DW40	Clinker1 + 0.9% SP4 + 6% G2	25.89		6.83	80% remain	1.4	97% remain		few drops

		T0	Test Description	T20	Test Description	T40	Test Description	T60	Test Description
DH1	Clinker2 (reference)	37.46	27% remain		few drops		few drops		no drops
DH2	Clinker2 + 0.2% SP1	30.36		17.73	70% remain	2.18	97% remain		few drops
DH3	Clinker2 + 0.5% SP1	13.83	segregate	15.64		20.58		19.6	
DH4	Clinker2 + 0.9% SP1	17.5	segregate	15.35		20.55		19.18	
DH5	Clinker2 + 0.2% SP2	21.93			87% remain	2.27	94% remain		few drops
DH6	Clinker2 + 0.5% SP2	15.61		20.32		34.72		40.49	
DH7	Clinker2 + 0.9% SP2	16.18	segregate	14.24	border on segregation	15.01		14.93	
DH8	Clinker2 + 0.2% SP3	16.75		37.52	12% remain	15.53	80% remain	3.4	95% remain
DH9	Clinker2 + 0.5% SP3	15.07		18.93		35.81		37.87	5% remain
DH10	Clinker2 + 0.9% SP3	13.66	segregate	13.64		15.47		16.49	
DH11	Clinker2 + 0.2% SP4	39.06			few drops		few drops		no drops
DH12	Clinker2 + 0.5% SP4	19.47		39.1	4% remain	3.75	93% remain	1.16	98% remain
DH13	Clinker2 + 0.9% SP4	13.23		14.56		18.23		30.26	
DH14	Clinker2 + 2% G1	45	10% remain	44.2	18% remain	8.03	85% remain	2.27	95% remain
DH15	Clinker2 + 4% G1	45.84	25% remain	17.95	65% remain	2.43	95% remain		drops only
DH16	Clinker2 + 6% G1	35.35	50% remain	7.9	88% remain	1.87	97% remain		few drops
DH17	Clinker2 + 0.2 SP1 + 2% G1	24.38		25.4		37.3		39.67	27% remain
DH18	Clinker2 + 0.9% SP1 + 2% G1	17.63	segregate	16.93	segregate	16.1	segregate	16.96	segregate
DH19	Clinker2 + 0.2 SP2 + 2% G1	42.09		43.18		43.58	30% remain	8.79	88% remain
DH20	Clinker2 + 0.9% SP2 + 2% G1	17.63		15.87		15.92		15.86	
DH21	Clinker2 + 0.2 SP3 + 2% G1	26.53		26.56		31.96		42.81	6% remain
DH22	Clinker2 + 0.9% SP3 + 2% G1	16.29		15.46		14.83		15.15	
DH23	Clinker2 + 0.2 SP4 + 2% G1	45.04	5% remain	43.7	12% remain	12.6	75% remain	3.66	96% remain
DH24	Clinker2 + 0.9% SP4 + 2% G1	29.78		37.09		44.86	8% remain	18.41	75% remain
DH25	Clinker2 + 0.2 SP1 + 6% G1	45.38		45.39	6% remain	13.89	78% remain		fast drops
DH26	Clinker2 + 0.9% SP1 + 6% G1	15.55	segregate	16.58	segregate	16.5	segregate	16.69	segregate
DH27	Clinker2 + 0.2 SP2 + 6% G1	47.69	8% remain	44.56	15% remain	10.84	88% remain		drops only
DH28	Clinker2 + 0.9% SP2 + 6% G1	17.69		14.95		15.01		15.83	
DH29	Clinker2 + 0.2 SP3 + 6% G1	49.47	35% remain	50.29	xx	44.78	30% remain	4.75	94% oor
DH30	Clinker2 + 0.9% SP3 + 6% G1	24.55		18.53		17.8		18.76	
DH31	Clinker2 + 0.2 SP4 + 6% G1	6.47	90% remain		drops only		few drops		no drops
DH32	Clinker2 + 0.9% SP4 + 6% G1	45.09	10% remain	27.38	55% remain		drops		few drops
DH35	Clinker2 + 2% G2	40.3	1% remain	35.12	45% remain	4.32	90% remain	1.06	98% remain
DH36	Clinker2 + 6% G2	40.07	2% remain	33.04	40% remain	3.38	94% remain	1.25	96% remain
DH37	Clinker2 + 0.9% SP1 + 6% G2	15.04	segregate	14.2	segregate	13.67	segregate	13.46	segregate
DH38	Clinker2 + 0.9% SP2 + 6% G2	13.67		13.24		13.07		13.01	
DH39	Clinker2 + 0.9% SP3 + 6% G2	13.93		13.41		13.23		13.63	
DH40	Clinker2 + 0.9% SP4 + 6% G2	14.23		16.76		19.87		25.29	
		T0	Test Description	T20	Test Description	T40	Test Description	T60	Test Description
SL1	Clinker3 (reference)	30.59	71% remain	3.68	83% remain	1.84	96% remain		few drops
SL2	Clinker3 + 0.2% SP1	29.81		34.04		41.01	10% remain	37.15	40% remain
SL3	Clinker3 + 0.5% SP1	24.95		25.08		26.46		29.52	
SL4	Clinker3 + 0.9% SP1	19.46		21.43		22.66		22.96	
SL5	Clinker3 + 0.2% SP2	32.1		37.15		42.6	11% remain	37.46	50% remain
SL6	Clinker3 + 0.5% SP2	22.32		22.61		25		28.11	
SL7	Clinker3 + 0.9% SP2	17.5	border segregation	17.75		18.27		18.75	
SL8	Clinker3 + 0.2% SP3	26.07		31.36		37.53	5% remain	38.8	38% remain
SL9	Clinker3 + 0.5% SP3	20.53		21.84		25.06		29.38	
SL10	Clinker3 + 0.9% SP3	16.67		16.46		16.96		18.04	
SL11	Clinker3 + 0.2% SP4	25.44	60% remain	4.61	87% remain	1.83	94% remain	0.94	99% remain
SL12	Clinker3 + 0.5% SP4	12.26	80% remain	5.67	87% remain	2.38	95% remain	1.64	97% remain
SL13	Clinker3 + 0.9% SP4	40.38	4% remain	38.58	17% remain	7.52	76% remain	1.74	96% remain
SL14	Clinker3 + 2% G1	44.8	8% remain	6.29	86% remain		fast drops		few drops
SL15	Clinker3 + 4% G1	12.53	80% remain	2.23	94% remain		few drops		no drops
SL16	Clinker3 + 6% G1	33.06	45% remain	2.04	96% remain		few drops		no drops
SL17	Clinker3 + 0.2 SP1 + 2% G1	43.6	2% remain	36.36	50% remain	2.16	96% remain		few drops
SL18	Clinker3 + 0.9% SP1 + 2% G1	16.41	segregate	16.35	segregate	16.53	segregate	16.86	
SL19	Clinker3 + 0.2 SP2 + 2% G1	31.5		41.63		30.78	48% remain	2.09	94% remain
SL20	Clinker3 + 0.9% SP2 + 2% G1	14	segregate	15.89	segregate	16.52	segregate	16.7	segregate
SL21	Clinker3 + 0.2 SP3 + 2% G1	22.86		30.06		44.9	8% remain	8.18	85% remain
SL22	Clinker3 + 0.9% SP3 + 2% G1	13.7	segregate	14.35	segregate	14.08	segregate	14.21	
SL23	Clinker3 + 0.2 SP4 + 2% G1	40.06	30% remain	3.76	92% remain		drops		no drops
SL24	Clinker3 + 0.9% SP4 + 2% G1	24.35		41.53	18% remain	3	93% remain		few drops
SL25	Clinker3 + 0.2 SP1 + 6% G1	45.84	26% remain	5.17	82% remain		few drops		no drops
SL26	Clinker3 + 0.9% SP1 + 6% G1	17.93	segregate	18.87	segregate	18.41	segregate	18.75	segregate
SL27	Clinker3 + 0.2 SP2 + 6% G1	47.88	15% remain	38.15	50% remain	0.84	98% remain		few drops
SL28	Clinker3 + 0.9% SP2 + 6% G1	16.43		15.4		15.9		17.1	
SL29	Clinker3 + 0.2 SP3 + 6% G1	27.67		31.4		40.95	25% remain	2.5	94% remain
SL30	Clinker3 + 0.9% SP3 + 6% G1	15.36		15.1		15.9		16	segregation start
SL31	Clinker3 + 0.2 SP4 + 6% G1	5.89	84% remain	0.83	98% remain		few drops		no drops
SL32	Clinker3 + 0.9% SP4 + 6% G1	29.46		33.66	25% remain	2.44	93% remain		few drops
SL35	Clinker3 + 2% G2	40.24	30% remain	1.63	94% remain		few drops		no drops
SL36	Clinker3 + 6% G2	39.06	10% remain	4.52	88% remain		few drops		no drops
SL37	Clinker3 + 0.9% SP1 + 6% G2	16.46	segregate	15.73	segregate	16.15	segregate	15.87	segregate
SL38	Clinker3 + 0.9% SP2 + 6% G2	16.7	segregate	15.8	segregate	15.38	segregate	16	segregate
SL39	Clinker3 + 0.9% SP3 + 6% G2	14.9	segregate	14.01	segregate	13.7	segregate	13.44	
SL40	Clinker3 + 0.9% SP4 + 6% G2	16.2		19.56		32.92		27.03	43% remain

## 11.3. Appendix D3; Setting time and Compression strength results

Mix Description	Code	Strength Test [Mpa]		Setting Times [seconds]	
		2 Day	7 Day	Initial	Final
Clinker1 (reference)	DWB 1	21.4	42.8	796	864
Clinker1 + 0.2% SP1	DWB 2	15.6	32.1	557	629
Clinker1 + 0.5% SP1	DWB 3	14.4	35.7	604	660
Clinker1 + 0.9% SP1	DWB 4	18.5	42.8	583	736
Clinker1 + 0.2% SP2	DWB 5	15.8	35.2	589	677
Clinker1 + 0.5% SP2	DWB 6	12.4	25.7	655	723
Clinker1 + 0.9% SP2	DWB 7	13.4	30.4	623	689
Clinker1 + 0.2% SP3	DWB 8	13.1	30.6	658	737
Clinker1 + 0.5% SP3	DWB 9	12.3	30.4	719	894
Clinker1 + 0.9% SP3	DWB 10	13.8	28.8	695	760
Clinker1 + 0.2% SP4	DWB 11	20.6	44.8	480	504
Clinker1 + 0.5% SP4	DWB 12	17.5	42.9	449	591
Clinker1 + 0.9% SP4	DWB 13	13.4	39.5	880	1022
Clinker1 + 2% G1	DWB 14	15.1	34.2	137	335
Clinker1 + 4% G1	DWB 15	25.5	45.0	136	193
Clinker1 + 6% G1	DWB 16	24.3	41.9	71	150
Clinker1 + 0.2 SP1 + 2% G1	DWB 17	16.0	33.4	175	262
Clinker1 + 0.9% SP1 + 2% G1	DWB 18	21.9	40.2	165	318
Clinker1 + 0.2 SP2 + 2% G1	DWB 19	19.1	37.5	139	162
Clinker1 + 0.9% SP2 + 2% G1	DWB 20	20.0	37.8	157	199
Clinker1 + 0.2 SP3 + 2% G1	DWB 21	15.4	34.5	153	238
Clinker1 + 0.9% SP3 + 2% G1	DWB 22	20.5	38.7	254	267
Clinker1 + 0.2 SP4 + 2% G1	DWB 23	14.1	34.8	142	184
Clinker1 + 0.9% SP4 + 2% G1	DWB 24	20.8	41.7	105	126
Clinker1 + 0.2 SP1 + 6% G1	DWB 25	24.3	41.2	87	263
Clinker1 + 0.9% SP1 + 6% G1	DWB 26	28.8	45.1	226	381
Clinker1 + 0.2 SP2 + 6% G1	DWB 27	24.2	41.6	129	198
Clinker1 + 0.9% SP2 + 6% G1	DWB 28	31.3	47.6	215	296
Clinker1 + 0.2 SP3 + 6% G1	DWB 29	22.3	38.9	121	345
Clinker1 + 0.9% SP3 + 6% G1	DWB 30	28.8	45.6	297	314
Clinker1 + 0.2 SP4 + 6% G1	DWB 31	24.0	42.0	77	144
Clinker1 + 0.9% SP4 + 6% G1	DWB 32	24.9	41.6	100	137
Clinker1 + 2% G2	DWB 35	16.3	34.4	143	249
Clinker1 + 6% G2	DWB 36	25.9	43.0	155	220
Clinker1 + 0.9% SP1 + 6% G2	DWB 37	33.0	48.5	288	354
Clinker1 + 0.9% SP2 + 6% G2	DWB 38	31.8	47.1	362	426
Clinker1 + 0.9% SP3 + 6% G2	DWB 39	31.3	47.0	345	390
Clinker1 + 0.9% SP4 + 6% G2	DWB 40	25.8	42.3	160	342

Mix Description	Code	2 Day	7 Day	Initial	Final
Clinker2 (reference)		32.0	49.9	122	181
Clinker2 + 0.2% SP1	DH 2	28.6	44.7	95	300
Clinker2 + 0.5% SP1	DH 3	33.3	49.8	160	405
Clinker2 + 0.9% SP1	DH 4	36.0	55.0	280	750
Clinker2 + 0.2% SP2	DH 5	25.7	42.5	105	345
Clinker2 + 0.5% SP2	DH 6	30.4	47.9	100	390
Clinker2 + 0.9% SP2	DH 7	34.1	55.5	190	355
Clinker2 + 0.2% SP3	DH 8	29.0	48.9	101	219
Clinker2 + 0.5% SP3	DH 9	32.0	51.6	130	258
Clinker2 + 0.9% SP3	DH 10	34.3	54.6	131	225
Clinker2 + 0.2% SP4	DH 11	32.0	52.4	126	239
Clinker2 + 0.5% SP4	DH 12	31.8	53.0	137	218
Clinker2 + 0.9% SP4	DH 13	32.1	51.2	150	251
Clinker2 + 2% G1	DH 14	24.7	43.5	120	192
Clinker2 + 4% G1	DH 15	34.3	46.1	104	157
Clinker2 + 6% G1	DH 16	38.3	50.1	56	79
Clinker2 + 0.2 SP1 + 2% G1	DH 17	23.5	40.8	128	187
Clinker2 + 0.9% SP1 + 2% G1	DH 18	33.0	45.6	169	242
Clinker2 + 0.2 SP2 + 2% G1	DH 19	23.4	41.0	147	183
Clinker2 + 0.9% SP2 + 2% G1	DH 20	33.5	49.8	235	294
Clinker2 + 0.2 SP3 + 2% G1	DH 21	22.5	42.0	145	209
Clinker2 + 0.9% SP3 + 2% G1	DH 22	28.5	46.6	208	287
Clinker2 + 0.2 SP4 + 2% G1	DH 23	24.6	42.8	102	163
Clinker2 + 0.9% SP4 + 2% G1	DH 24	27.2	44.1	135	194
Clinker2 + 0.2 SP1 + 6% G1	DH 25	40.5	51.8	55	88
Clinker2 + 0.9% SP1 + 6% G1	DH 26	41.5	51.4	130	195
Clinker2 + 0.2 SP2 + 6% G1	DH 27	39.2	51.2	85	135
Clinker2 + 0.9% SP2 + 6% G1	DH 28	44.4	53.0	185	258
Clinker2 + 0.2 SP3 + 6% G1	DH 29	39.9	52.2	76	119
Clinker2 + 0.9% SP3 + 6% G1	DH 30	46.0	54.9	150	257
Clinker2 + 0.2 SP4 + 6% G1	DH 31	39.6	50.2	39	91
Clinker2 + 0.9% SP4 + 6% G1	DH 32	43.0	51.3	73	111
Clinker2 + 2% G2	DH 35	27.3	46.8	130	155
Clinker2 + 6% G2	DH 36	41.9	51.4	110	171
Clinker2 + 0.9% SP1 + 6% G2	DH 37	43.1	53.6	236	293
Clinker2 + 0.9% SP2 + 6% G2	DH 38	47.4	56.3	281	364
Clinker2 + 0.9% SP3 + 6% G2	DH 39	44.8	54.3	239	362
Clinker2 + 0.9% SP4 + 6% G2	DH 40	45.0	52.9	187	226



Mix Description	Code	2 Day	7 Day	Initial	Final
Clinker3 (reference)		19.0	34.5	598	860
Clinker3 + 0.2% SP1	SL 2	15.5	28.9	597	780
Clinker3 + 0.5% SP1	SL 3	16.7	29.6	593	795
Clinker3 + 0.9% SP1	SL 4	18.8	33.3	685	837
Clinker3 + 0.2% SP2	SL 5	15.8	28.9	549	764
Clinker3 + 0.5% SP2	SL 6	15.3	26.6	626	856
Clinker3 + 0.9% SP2	SL 7	16.7	18.2	818	1021
Clinker3 + 0.2% SP3	SL 8	15.7	29.0	566	819
Clinker3 + 0.5% SP3	SL 9	15.0	29.6	621	824
Clinker3 + 0.9% SP3	SL 10	16.7	33.3	750	1050
Clinker3 + 0.2% SP4	SL 11	20.4	35.8	666	921
Clinker3 + 0.5% SP4	SL 12	17.9	34.2	630	923
Clinker3 + 0.9% SP4	SL 13	16.1	32.3	925	1108
Clinker3 + 2% G1	SL 14	22.7	37.2	148	242
Clinker3 + 4% G1	SL 15	21.7	34.1	129	173
Clinker3 + 6% G1	SL 16	22.4	33.8	93	152
Clinker3 + 0.2 SP1 + 2% G1	SL 17	20.3	34.1	191	232
Clinker3 + 0.9% SP1 + 2% G1	SL 18	22.9	37.3	214	287
Clinker3 + 0.2 SP2 + 2% G1	SL 19	21.3	35.0	167	225
Clinker3 + 0.9% SP2 + 2% G1	SL 20	23.9	36.1	301	345
Clinker3 + 0.2 SP3 + 2% G1	SL 21	20.7	34.5	196	278
Clinker3 + 0.9% SP3 + 2% G1	SL 22	22.8	37.4	342	441
Clinker3 + 0.2 SP4 + 2% G1	SL 23	23.5	37.2	145	271
Clinker3 + 0.9% SP4 + 2% G1	SL 24	20.6	34.5	221	331
Clinker3 + 0.2 SP1 + 6% G1	SL 25	20.8	30.6	93	153
Clinker3 + 0.9% SP1 + 6% G1	SL 26	27.8	39.0	181	205
Clinker3 + 0.2 SP2 + 6% G1	SL 27	21.4	31.5	138	192
Clinker3 + 0.9% SP2 + 6% G1	SL 28	26.7	38.4	227	284
Clinker3 + 0.2 SP3 + 6% G1	SL 29	20.7	32.2	138	212
Clinker3 + 0.9% SP3 + 6% G1	SL 30	24.8	36.8	264	319
Clinker3 + 0.2 SP4 + 6% G1	SL 31	22.7	34.6	89	135
Clinker3 + 0.9% SP4 + 6% G1	SL 32	22.9	33.7	145	209
Clinker3 + 2% G2	SL 35	23.6	36.5	144	211
Clinker3 + 6% G2	SL 36	23.4	34.3	155	245
Clinker3 + 0.9% SP1 + 6% G2	SL 37	27.0	37.8	248	307
Clinker3 + 0.9% SP2 + 6% G2	SL 38	27.7	37.3	309	334
Clinker3 + 0.9% SP3 + 6% G2	SL 39	26.2	37.8	341	379
Clinker3 + 0.9% SP4 + 6% G2	SL 40	22.9	33.2	209	261