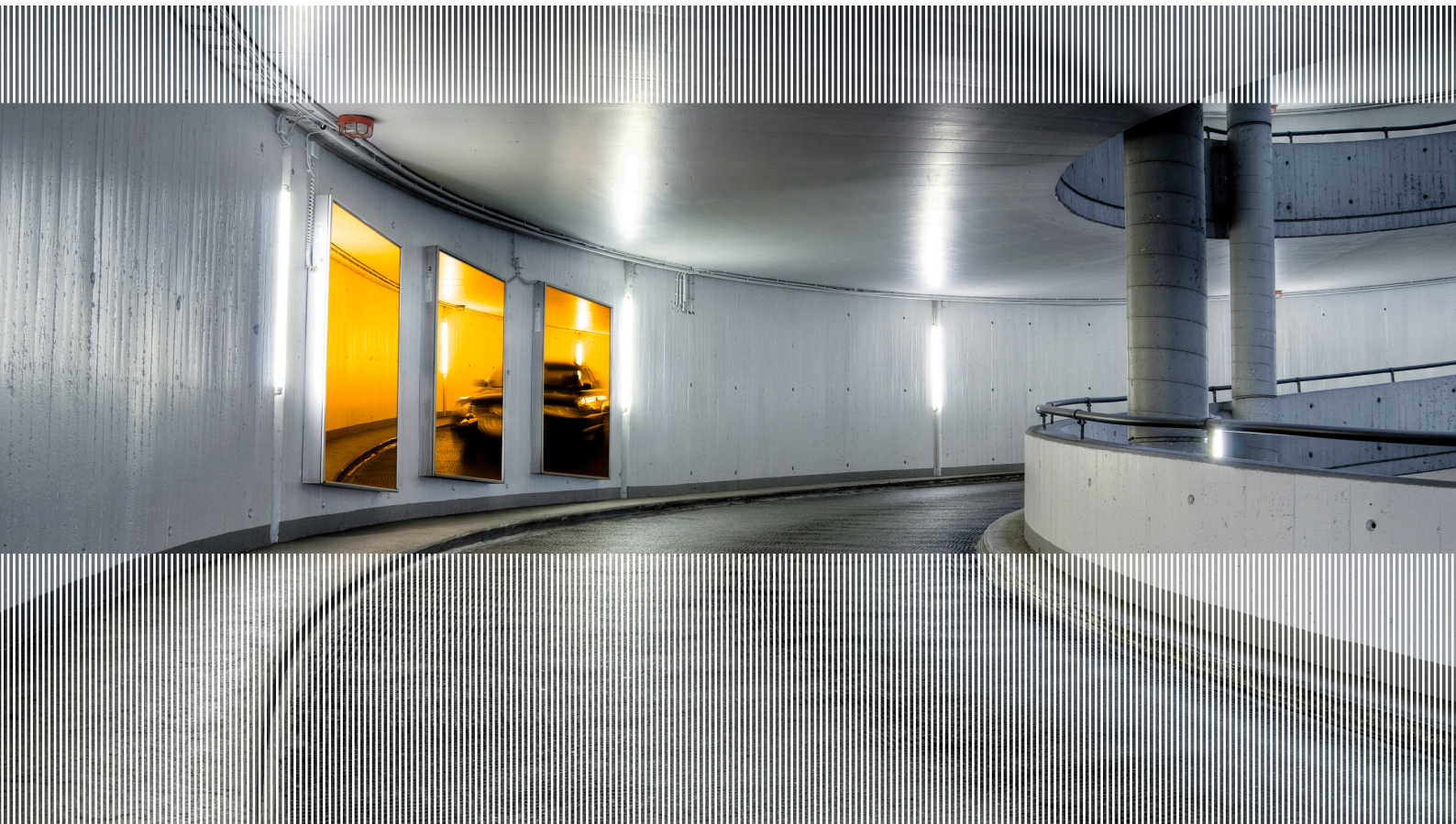**SINTEF Building and Infrastructure**   Serina Ng

Characterisation of fillers with plasticizers:
Zeta Potential measurements

COIN Project report 61 – 2015

SINTEF Building and Infrastructure

Serina Ng

Characterisation of fillers with plasticizers: Zeta Potential measurements

FA: Competitive constructions

SP 2.3 Production of high quality manufactured aggregate for concrete

COIN Project report 61 – 2015

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Preface

This study has been carried out within COIN - Concrete Innovation Centre - one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently eight projects in three focus areas:

- Environmentally friendly concrete
- Economically competitive construction
- Aesthetic and technical performance

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %).

For more information, see www.coinweb.no

Tor Arne Hammer
Centre Manager

Summary

The zeta potentials of five different fillers and three commercial plasticizers were explored in this report. The main purpose was to determine how these materials interact with each other to aid dispersions, in an effort to explain the macroscopic observations of sedimentations and interactions of fines in crushed aggregates with plasticizers. The investigation of the materials is divided into 2 areas and they will be summarized as below:

Area 1 – Understanding of sedimentation observation through zeta potential studies

Three different sets of systems were explored: - cement alone, filler alone and cement/filler. In the cement system, regardless of plasticizers presence, the zeta potential was positive due to the high content of Al containing clinker phases in cement employed, and the ability to form double layer during surface adsorption by the cement particles. For fillers only system, the two fillers, limestone 2 and natural sand possessed differently charged surfaces, which were very close to isoelectric point. This indicated that they are relatively unstable and can flocculate easily. Upon adding to cement pore solution, stability of the system improved while a charge reversal was observed, attributing to the adsorption of ions from the pore solution onto the surfaces of the filler particle. There, it was found that the dispersing effectiveness by plasticizers can be a factor of both the stability of slurry (magnitude of zeta potential value) and the adsorbed amount of lignosulfonate as described by the change in zeta potentials.

Lastly, in the cement/filler combination system, the adsorption of plasticizers by fillers in presence of cement is dependent on the type of plasticizers present. MapaPlast is adsorbed rapidly by both fillers and cement due to its inherent high negative charge. In the case of SP-130, preferential adsorption appears to favour cement in the presence of limestone 2, whereas competitive adsorption is present when natural sand is mixed with cement. The large zeta potential value of pastes containing MapaPlast as compared to those with SP-130 indicated that the former system is more stable, whereby the tendency to undergo flocculation is lower.

In general, adsorption of plasticizers by the particles – fillers or cement is a rapid process.

Area 2 – Understanding of the behaviour of SXN in three selected filler obtained from crushed aggregates

Three different fillers; a limestone (different from that from **Area 1**), an anorthosite and a quartzite were investigated. One plasticizer, SXN was employed here. When the zeta potentials of the fillers were studied alone, all three fillers displayed very different zeta potentials when measured in the cement pore solution. Anorthosite registered a very positive zeta potential of +12.4mV, limestone 0.0mV and quartzite -3.4mV. These results indicate that limestone has the highest tendency flocculate when left alone, whereas anorthosite is the most stable.

When SXN was added, the interaction between the plasticizers and fillers differed. With anorthosite, rapid consumption which plateau at around 0.5%bwoc of SXN added. Limestone is a gradual process with preferential adsorption of polycarboxylate based polymers with shorter side chains, whereas quartzite is more unpredictable in terms of adsorption. However, it seems that quartzite prefer polymers with longer side chain. Stability of the systems is greatest for anorthosite

system, but the degree of adsorption and dispersion cannot be purely measured by the zeta potential due to the steric effect of the long side chain from the polycarboxylate based polymers SXN, particularly in the case of quartzite.

Table of contents

1   Introduction

1.1   Principal objectives and scope

The purpose of this work is to investigate the effect of different plasticizers on the zeta potentials of selected fillers in two different cementitious systems. For this, the work is divided into 2 parts; **Area 1** and **Area 2**.

In **Area 1**, the immediate zeta potential values of slurry systems in presence or absence of plasticizers will be measured. This will be done under the following conditions:

  (1) Filler only in deionised water (measure inherent characteristics of the fillers)
  (2) Filler only in cement pore solution
  (3) Filler in cement pore solution, with pre-dissolved plasticizer
  (4) Filler/cement combination in deionised water, with pre-dissolved plasticizer

All plasticizers are introduced as direct addition.

In **Area 2**, the zeta potential of three fillers and the effect of adding a plasticizer, SXN as a function of time is to be investigated. This thus includes:

  (1) Measurement of zeta potential of the three fillers in cement pore solution
  (2) Titration of SXN as a function of time to each filler slurry

All plasticizers are introduced as delayed addition.

1.2   Background

This investigation was conducted with the aim to utilize zeta potential measurements as a technique in describing and understanding the physical properties of concrete systems through models of dispersions at a nanoscale level. At high solid fraction, the influence of surface forces dominates the behaviour of powders and suspensions relative to body forces which can be correlated to body mass. In this way, coupled to the influence of admixtures present in the system, complicated colloidal interactions could arise, including and not limited to flocculating effects [1]. It is postulated that the flocculation and thus extent of dispersion in the system can be derived from the change in zeta potential. Under the electrostatic influence, particles possessing similar charges would repel and be dispersed, thus reducing flocculation, whereas on the other side of spectrum, dissimilarly charged particles would attract and cause precipitation. In presence of non-ionic polymers, steric hindrance would lessen the impact of inter-particle electrostatic attraction. With this in mind, it was thus promoted to perform zeta potential measurements on selected filler systems in presence and absence of plasticizers to understand better the driving force behind their interactions and thus macroscopic observations. The area of focus can be divided into two, which is termed as **Area 1** and **Area 2** in this report.

Area 1 focuses on deriving a mechanistic explanation at the interfacial level for the stabilizing effects of fillers or a combination of fillers and plasticizers on the concrete as determined through the study of the sedimentation process with HYdroStatic Pressure Test (HYSPT) and the total bleeding of cement matrices [2]. It was found that slurry containing coarse natural sand filler displayed lower sedimentation rate but more bleeding than the fine limestone filler. This was accounted for by the flocculation of the powders which can give rise to reduced stability effect from filler addition or replacement. However, the addition of

plasticizers complicates matter and unpredictable variations in sedimentation rates and bleeding was observed. Therefore, zeta-potential measurements on solutions with the same fillers and plasticizer were proposed to be conducted to study the inter-particles forces and different flocculation states.

In **Area 2**, the focus is on the interaction of plasticizers with fines from crushed aggregates. It was found in the COIN project FA 2.3 Manufactured crushed aggregates that such fines influence not only the workability and behaviour of concrete, but also the performance of admixtures such as superplasticizers added. It was determined that many factors play a role in this, including and not limited to particle size, shape, grading, texture, etc. The aim of the work here is thus to investigate the influence of surface charges through zeta potential measurements on the interaction between three selected fillers and a well-balanced commercial plasticizer, SXN. The three fillers were selected based on their differences in the influence on their rheological effects on matrixes.

1.3   Principle of zeta potential measurements

In solution, the presence of a net charge on a particle affects the distribution of ions surrounding the particle, resulting in an increase in the concentration of counter-ions. The region over which this influence extends is called the electrical double layer. As defined by the name, the electrical double layer exists as two separate regions: The inner region (Stern layer) consists of strongly bound ions, whilst the outer region (diffuse layer) consists of loosely associated ions. As the particle moves through solution, due to gravity or an applied voltage, the ions move with it. At some distance from the particle exists a 'boundary' beyond which ions do not move with the particle. This is known as the surface of hydrodynamic shear, or the slipping plane, and exists somewhere within the diffuse layer. It is the potential that exists at the slipping plane that is defined as the zeta potential. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle (**Figure 1**).
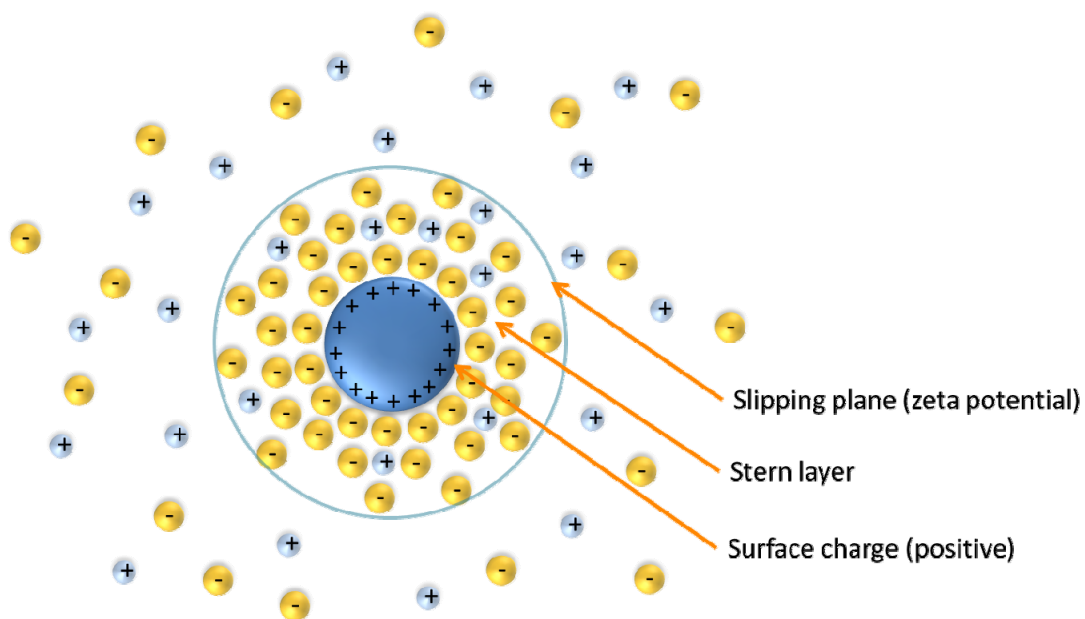
Figure 1 Schematic illustration of electric double layer and zeta potential

All particles in suspension exhibit a zeta potential, or surface charge due to their ionic characteristics and dipolar attributes. In liquids, the surfaces often bind layers of molecules or ions or polyelectrolytes. This results in a deviation of the slipping plane from the solid-liquid interface. The measurement and knowledge of zeta potential is critical for optimizing processing, predicting interactions and formulation stability. Furthermore, zeta potential can be used as a simple method for quality control. Methods for measuring a particle's zeta potential are dependent on the nature of both the particle and the suspension formulation.

Zeta potential is crucial in determining the stability of a colloidal suspension; for colloidal stability the repulsive forces must be dominant i.e. the greater the zeta potential the more likely the suspension is stable. If the zeta potential is low the tendency for flocculation is increased. Generally, when the net charge of particle is zero, the suspension is usually highly unstable, and the occurrence of flocculation is at the highest.

In this investigation, quantification of the zeta potential of the particles in suspension was performed by the electroacoustic method applying a model DT 1200 Electroacoustic Spectrometer from Dispersion Technology, Inc. (Bedford Hills, NY/USA). The principle is based on ultrasound propagation through the medium, resulting in an electroacoustic phenomenon called colloid vibration current, from which the zeta potential is then calculated. The electroacoustic technique characterizes the dynamic mobility of particles in suspension. Typically this technique is used to measure stable suspensions of small particles (1nm to 10μm). A high frequency (~106 HZ) electric field is applied to the samples, causing charged particles to oscillate, and to produce a sound wave of the same frequency. The oscillation (dynamic mobility) of the particles is described by its magnitude and phase angle (how far the particle motion lags behind the applied field). The sound wave is detected and analyzed to determine the motion of the particles.

The main advantage of this technique over 'traditional' electrophoretic machines is the ability to measure zeta potential in slurries of greater than 10wt% solids concentration (up to 60wt% depending on the sample).

2   Experimental

The experiments conducted in this report can be divided into 2 areas; **Area 1** and **Area 2** respectively. In **Area 1**, the focus is on point measurements, whereby zeta potential of the fillers in presence or absence of plasticizers was to be determined immediately after homogeneous mixing of the wetted samples. The latter focuses on the effect of addition of plasticizers on the zeta potential of fillers as a function of time. The difference between the two areas is thus direct (**Area 1**) and delayed (**Area 2**) addition of the plasticizers. Additionally, as the purpose of studying each area differed, the materials employed differed between them too. The description of the experimental and materials employed in each area will be highlighted here.

2.1   Materials

A total of five fillers, three plasticizers and two cements were employed in the two studies in this investigation. The fillers included two types of limestone, natural sand supplied from quarry in Årdal (Norway), a quartzite and an anorthosite. The three plasticizers were all supplied from Mapei in Norway and were MapaPlast, SP-130 and SXN. MapaPlast is based on lignosulfonate chemistry, whereas the latter two were polycarboxylate based superplasticizers. SP-130 contains one polycarboxylate based polymer with long side chain, whereas SXN possess two such polymers; one with long side chain and the other short side chains. The cements were provided by Norcem, Norway and they were standard cements (without cementitious supplementary materials, SCM) and standard fly ash cement respectively. **Table 1** displays the materials that were utilized in each area of research as mentioned in the introduction. The relevant particle size (D_{50} and D_{84} respectively) of the cements and fillers for zeta potential measurements are recorded in **Table 2**.

Table 1 Division of materials according to research area

Material type	Area 1	Area 2
Cement	Standard	Standard fly ash
Fillers	Limestone 2 Natural sand (Årdal)	Limestone 1 Quartzite Anorthosite
Plasticizers	MapaPlast SP-130	SXN

Table 2 PSD of cements and fillers samples employed in this investigation

Material	D_{50} [μm]	D_{84} [μm]
Standard cement	13.3	31.0
Standard FA cement	10.5	49.8
Anorthosite	10.1	20.2
Limestone 1	8.8	18.1
Limestone 2	18.0	51.2
Natural sand (Årdal)	50.2	101.0
Quartzite	10.0	19.8

2.2   Preparation of samples for measurements

Samples were prepared in both cement pore solution and deionised water. The cement pore solution was obtained by filtering (1) standard cement slurries, (2) filler slurries or (3) cement + filler slurries with a buchner funnel and pump setup. These three pore solutions will be termed as Cem-PS, F-PS and CF-PS for the rest of document for simplification. The pore solution was stored under vacuum before utilization in zeta potential measurements to

decrease carbonation of the solution, whereas the w/c of the cement slurry was 0.5. For each batch of pore solution, 400g of dry powder was employed to minimize any systematic error which could arise as a result of differences in suction force on sample based on the amount of sample present. The yield of pore solution per batch of suction filtration was less than 100g.

Prior to zeta potential measurements, all dry powders (cement and fillers when applicable) were weighed out in a 50ml PE tube. The total amount of dry powder for each preparation was kept at a constant amount of 50g (**Area 1**) and 10g (**Area 2**). To the dry powder, water or pore solution at the desired water to filler ratio (w/fi) was added and sample was mixed on vortex for 15s. The homogenized mixture was subsequently poured into a 15mL beaker, where zeta potential values were measured within 3min after wetting. When required, the plasticizers were mixed into the solution before it is added to the dry powder.

The amount of materials and the type of medium (water or pore solution) employed for each generic measurement can be found in **Table 3** and **Table 4** for the respective areas of research. The conditions employed in **Area 1** corresponded to parameters employed in the HYdroStatic Pressure Test (HYPT) performed in a separate study [2], whereas that for **Area 2** was generic to determine the general surface behavior of the selected fillers in presence of plasticizer SXN. However, to keep the findings actual, realistic conditions were employed in this study. The w/c of the cement was kept at 0.5 when preparing the cement pore solution. The amount of filler added was calculated based on the fi/c as given from other studies. High concentration of filler was not used in this study to prevent excessive sedimentation of particles which could affect the zeta potential measurements.

Table 3 Area 1: Amount of materials and medium employed for zeta potential measurements

No.	Cement	Filler	Plasticizer^	w/c	w/fi	Medium	Background
		[g]					
1	50	-	-	0.5	-	water	Cem-PS
2	50	-	0.3	0.5	-	water	Cem-PS
3	-	50	-	-	0.57	water	F-PS
4	-	50	-	0.5*	0.57	Cem-PS	CF-PS
5	-	50	0.3	0.5*	0.57	Cem-PS	CF-PS
6[NS]	33.2	16.8	-	0.67	1.49	water	CF-PS
7[NS]	33.2	16.8	0.3	0.67	1.49	water	CF-PS
8[LS]	20.9	29.1	-	0.83	0.86	water	CF-PS
9[LS]	20.9	29.1	0.3	0.83	0.86	water	CF-PS

^amount of plasticizers used is by dry mass content
*w/c used to produce Cem-PS as medium for system
-Fillers refer to both limestone 2 and natural sand

Table 4 Area 2: Amount of materials and medium employed for zeta potential measurements

No.	Filler type	Filler	Plasticizer^	w/c	fi/c	Medium	Background
		[g]					
1	Quartzite	10	-	0.5	0.112	Cem-PS	F-PS
2	Anorthosite	10	-	0.5	0.130	Cem-PS	F-PS
3	Limestone 1	10	-	0.5	0.124	Cem-PS	CF-PS
4	Quartzite	10	Titration	0.5	0.112	Cem-PS	CF-PS
5	Anorthosite	10	Titration	0.5	0.130	Cem-PS	CF-PS
6	Limestone 1	10	Titration	0.5	0.124	Cem-PS	CF-PS

^amount of plasticizers used is by dry mass content

2.3   Zeta potential measurements

Zeta potentials of the suspensions made of fillers and/or cement prepared in the presence or absence of plasticizers were determined using a model DT 1200 Electroacoustic Spectrometer from Dispersion Technology, Inc. (Bedford Hills, NY/USA). Prior to all measurements, the ionic vibration current (IVI) of a prepared solution (background in **Table 3** and **4**) is measured to cancel out influence of the medium on the colloidal vibration current (CVI) of the sample, which will give the zeta potential of the colloidal system.

During all measurements, the amount of sample in the beaker was ensured to have a minimum height whereby the zeta probe is submerged to a depth of at least 1cm for accurate measurements. Additionally, constant stirring with a magnetic stirring bar in the beaker was present. The zeta probe was placed at least 1~2cm away from the stirring bar during measurements to minimize the disturbance due to vortexing of the suspension.

For **Area 1**, all samples were prepared and measured within 3 minutes of wetting to ensure that the immediate zeta potentials of the systems are captured. Thereafter, measurements are continued for a further 10 minutes to determine the stability of the suspensions.

For **Area 2**, filler samples suspended in Cem-PS were measured first (sample no. 1 to 3 in **Table 4**). The stability of these particles is determined over a period of 1h. Therefore, titration of SXN was performed, at a rate of 0.2ml a SXN polymer solution with a solid content of 19%. Measurements were stopped when 10ml of SXN was titrated, which took approximately 1.5h.

3   Results and discussion

This chapter will be divided into two main chapters; **Area 1** and **Area 2** respectively. **Area 1** focuses on the immediate zeta potential values of slurry systems in presence or absence of plasticizers. The slurries consist of cement alone, filler alone or a combination of cement and filler. For **Area 2**, the purpose is to determine the effect of increasing dosage of SXN on the zeta potentials of three selected fillers by titration. In this way, the amount of SXN adsorbed could be determined to a certain extent.

 The chapters will be subdivided into relevant sections for elaboration of results. At the onset of this chapter, it is important to emphasize that the surfaces of particles in suspensions such as cements are generally heterogeneous (**Figure 2**). Therefore, the zeta potential observed for each system is simply an overall zeta potential of the particles present.
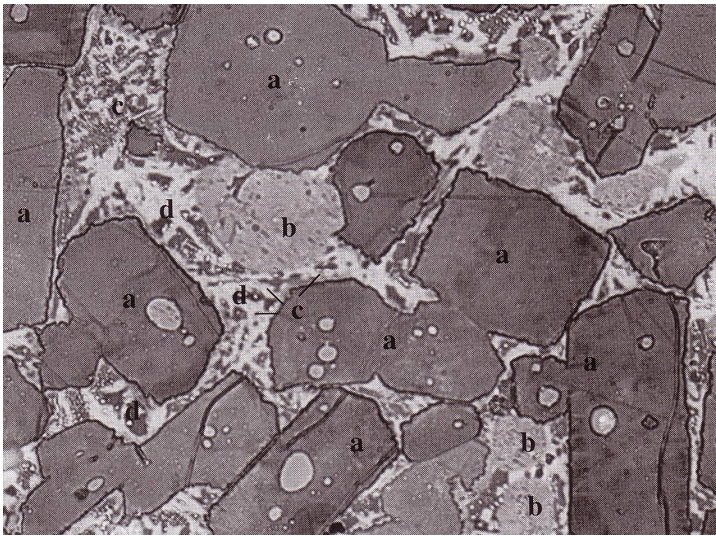
Figure 2 Polished sample showing the heterogeneity of cement particles; a = C_3S, b = C_2S, c = C_3A and d = C_4AF (c and d form the interstitials)

3.1   Area 1

This area focuses on the immediate zeta potential values of slurry systems in presence or absence of plasticizers. The slurries consist of cement alone, filler alone or a combination of cement and filler.

3.1.1 Overview of all results

All zeta potential measurements of the suspensions are presented in **Table 5**. In general, cement samples displayed positive zeta potentials in presence or absence of plasticizers, regardless of the type of plasticizers added. On the other hand, the zeta potential of fillers only or even when cement is mixed into the system, varied depending on the type of environment or plasticizers added.

For clarity, the list of results will be divided into 3 different sections; (I) cement alone, (II) fillers, both limestone and natural sands and (III) fillers + cements. More in-depth description and potential explanation for the zeta potential values will be presented there. Additionally, the results shown in this table will be repeated graphically in each section.

Table 5 Compilation of zeta potentials of the different systems tested

No.	System	Zeta potential [mV]	Φ	w/c
1	Cement only	+ 2.2	0.388	0.5
2	Cement + MapaPlast	+ 2.9	0.388	0.5
3	Cement + SP-130	+ 2.7	0.388	0.5
4	Limestone 2 (water)	+ 0.8	0.388	0.57
5	Limestone 2 (Cem-PS)	- 2.9	0.388	0.57
6	Limestone 2 + MapaPlast (Cem-PS)	- 7.6	0.388	0.57
7	Limestone 2 + SP-130 (Cem-PS)	- 1.2	0.388	0.57
8	Natural sand (water)	- 0.5	-*	0.57
9	Natural sand (Cem-PS)	+ 3.5	-*	0.57
10	Natural sand + MapaPlast (Cem-PS)	- 5.5	-*	0.57
11	Natural sand + SP-130 (Cem-PS)	- 3.0	-*	0.57
12	Natural sand + cement + MapaPlast	- 3.9	0.442	0.5
13	Natural sand + cement + SP-130	- 1.8	0.442	0.5
14	Limestone 2 + cement + MapaPlast	- 4.5	0.388	0.5
15	Limestone 2 + cement + SP-130	+ 0.2	0.388	0.5

*Solid fraction of samples not defined. The samples were prepared according to mass of fillers added in samples no. 4 to 7.

3.1.2 Cement with plasticizers

Figure 3 presents the zeta potentials of cement slurries, with or without plasticizers. The zeta potential of a pure cement paste prepared at a w/c of 0.5 was + 2.2 mV. This could be explained potentially by the heterogeneity of the cement particles, which in our case, more positively charged clinker phases could be found on the surfaces of the cement particles. Another reason for this positive charge can be attributed to the rapid hydration of C_3A in presence of gypsum. Standard cement generally contains ~7% of C_3A. Hydration of this clinker phase lead to the formation of CAH compounds which generally carry a positive zeta potential, e.g. ettringite was found to possess a zeta potential value of +4.15 mV, while monosulfate +2.84mV [3]. The positive zeta potential value of the cement slurry indicated that it will have a preference to act as a docking site for incoming anionic polymers such as plasticizers.
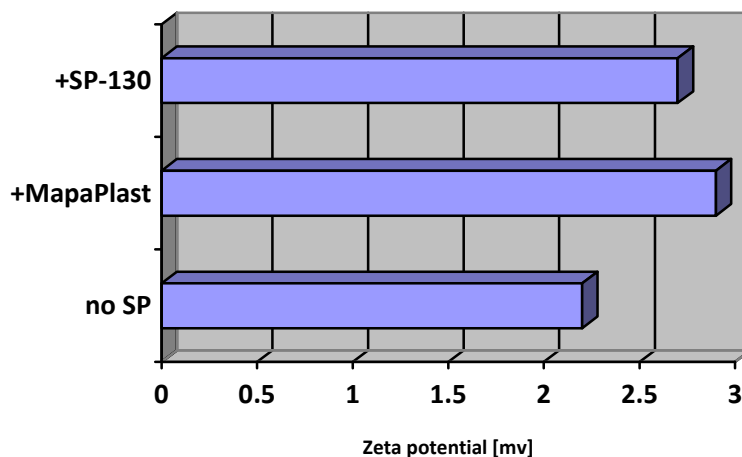

Figure 3 Zeta potentials of cement alone, with MapaPlast and SP-130 respectively

In the presence of plasticizers, the zeta potential increased slightly to more positive values. This may appear surprising at first as adsorption of anionic polymers onto the positive surface of cement particles should generally decrease the zeta potential of the particles as a

result of increase stern layer which diffuses the positive zeta potential, and in turn is subsequently replaced by the negative charges exerted by anchored polymers.

A plausible hypothesis for this observation could be linked to the negative nature of the plasticizers and abundant cations in cement pore solutions. When the plasticizers adsorb onto the cement grain, a rapid reversal of charge on the surface occurred. However, due to the rapid dissolution of clinkers, especially C_3A in solution, a constant supply of cations such as Ca^{2+} are released and are available in the solution. The presence of negative plasticizers on the cement particles mask their positive surfaces, turn it negative and promotes adsorption of cations onto the polymer, forming a double layer (**Figure 4**). This is supported by the fact that the cement slurry with the more anionic MapaPlast showed a higher zeta potential value than that with SP-130.

A point to note here is that for hypothesis to be valid, adsorption of plasticizers onto cement grains need to be a very rapid process, so that cations could react with the negative surface before being consumed in other reactions. Therefore, it could be assumed that the plasticizers tested here interact and are adsorbed onto the surfaces of standard cement very rapidly.
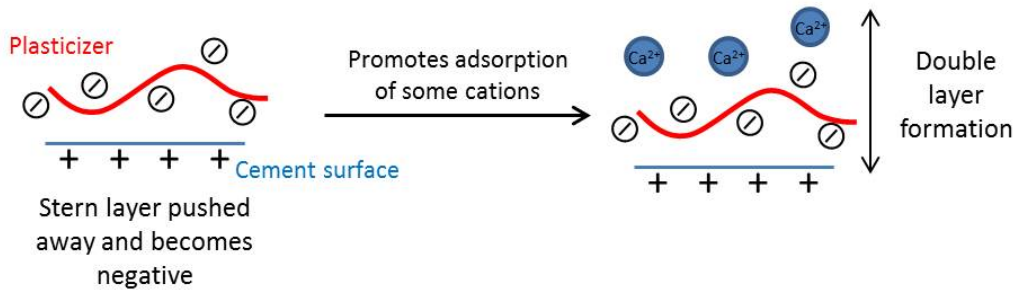
Figure 4 Formation of double layer, rendering zeta potential of cement with added plasticizers to be positive

3.1.3 Limestone and natural sand alone

Suspended fillers alone were tested, both in presence and absence of plasticizers. To qualify the fillers, they were tested in deionised water, to determine the innate surfaces of these particles. As observed in **Figure 5**, limestone 2 has a positive zeta potential value of +0.8mV, whereas natural sand was negative at -0.5mV. The zeta potentials of these two fillers are relatively close to zero, rendering them less ionic stable as compared to the cement particles and more susceptible to flocculation. However, the tendency for more anionic or ionic electrolytes or molecules from solution is still present. This can be observed by the high reversal of charge when both fillers were added to the cement pore solution. This phenomenon can be explained by the adsorption of ions (Ca^{2+} and SO_4^{2-} most likely) onto the charged surfaces of the fillers. It should however, be noted that in these static filler systems here, the availability of electrolytes from the cement pore solution to adsorb onto the surfaces is depleted after initial adsorption, unlike that in the case of cement.

When plasticizers are added, both fillers displayed negative zeta potentials, whereby the zeta potentials of the slurries with MapaPlast were more negative than that with SP-130. This can be accounted for by the fact that MapaPlast is more anionic as compared to SP-130. Additionally, due to the non-replenishing nature of the cement pore solution, double layer formation such as in the case of cement slurry (see **Figure 4**) was not significant enough such as in section 3.1.2, causing the systems to possess negative zeta potential values after addition of plasticizers.

When comparing the impact of plasticizers on the two fillers, it is interesting to note that the different plasticizers exerted different effects. In presence of MapaPlast, the limestone 2 slurries displayed a more negative zeta potential value (-7.6mV) than when natural sand (-5.5mV) was present. This may be attributed to the initial zeta potentials of the fillers, whereby after adsorption resulted in an overall less negative zeta potential in natural sand than limestone 2. However, the change in zeta potential is much greater in the case of natural sand (ΔZP = 9mV) than limestone 2 (ΔZP = 4.7mV), indicating a higher amount of lignosulfonate is adsorbed by the natural sand than limestone 2, thus leading to potentially a better dispersion of the former.
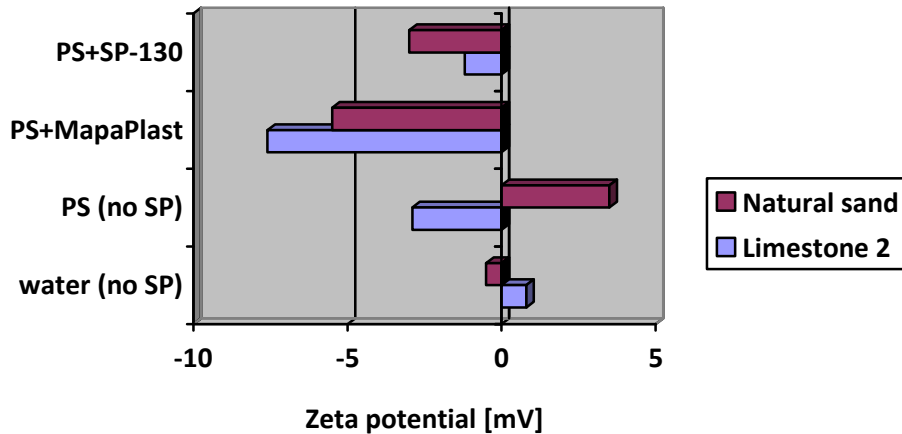
Figure 5 Zeta potentials of limestone 2 and natural sands in water or pore solution (PS), in presence or absence of plasticizers

It should be noted at this instance that it has been postulated that adsorption of lignosulfonate onto cement particles occurs in an orientation whereby lignosulfonate is a flat disc, adsorbing parallel to the surface of cement particles. Therefore, in such a situation, the large lignosulfonate molecule could potentially mask the 'free surfaces' of the cement particles, rendering the overall zeta potential unpredictable.

However, what is important here is the overall stability of the fillers in the polyelectrolyte rich medium. In general, the higher the zeta potential value (negative or positive), the more stable the suspension will be due to better dispersion, thus rendering limestone 2 with MapaPlast to be more stable than that of natural sand. However, due to the higher adsorbed amount of lignosulfonate by natural sand which can aid in dispersion, dispersion of both systems may thus be of similar magnitude.

In the addition of SP-130, the zeta potential value of natural sand slurry is more negative than that of limestone 2. This could be explained by the lower charge of such polycarboxylate based plasticizers. In such cases, preferred adsorption of SP-130 will occur on the more positive surface of natural sand, thus giving a higher overall reversal of charge. This explanation could be clarified by performing adsorption investigations by e.g. total organic carbon (TOC) analysis, whereby the amount of plasticizers adsorbed by each filler could be clarified. Here, the ΔZP of natural sand system is also greater than that of limestone 2. However, care should be taken when giving direct correlation of zeta potential results to adsorbed amounts of SP-130 due to the steric effect exerted by the side chains of the polycarboxylate polymers in SP-130, which can diffuse and extend the stern layer and alter the final zeta potential value registered.

3.1.4 Filler with cement in presence of plasticizers

The last set of results in **Area 1** relates to the zeta potentials of the combination of fillers and cement in a slurry. The results for the four systems investigated are presented in **Figure 6**. In general, the zeta potential of cement/filler slurry is a result of the overall surface charge of both cement and filler in the system. In presence of plasticizers, the cement and fillers will compete with each other for adsorption of the plasticizer, which will effectively vary the zeta potential of the particulate system.
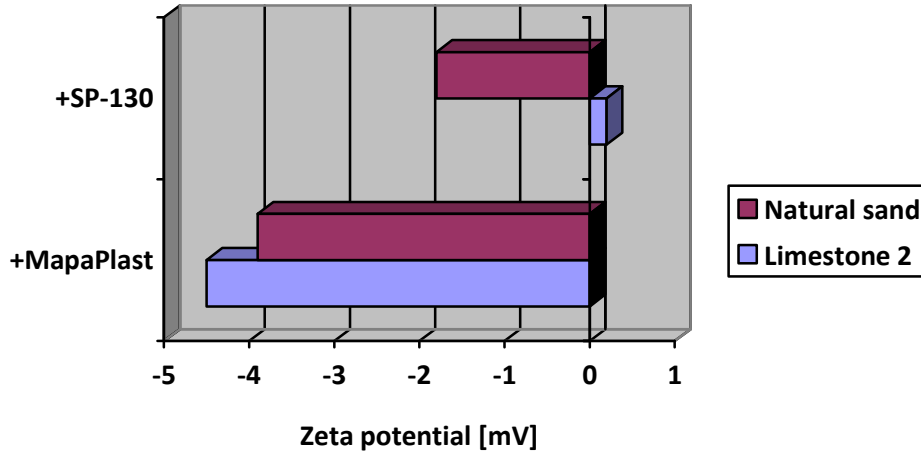
Figure 6 Zeta potentials of a combination of filler and cement systems in PS, in presence of MapaPlast or SP-130

As predicted, the zeta potentials of the slurries in presence of MapaPlast were negative. This, as before can be attributed to the negative charge of the MapaPlast, which can adsorb rapidly onto the surfaces of the particles in the slurry. The zeta potentials registered are lower than that for pure filler systems due to the inherent positive nature of the cement slurry. The negative zeta potential also indicates that adsorption of MapaPlast occurred rapidly onto fillers too (similar to cement), thus allowing both fillers to be negative (see natural sand).

When SP-130 was added, the variation in zeta potentials between the two slurries was greater, whereby natural sand registered a negative zeta potential value of -1.8mV, whereas limestone 2 displayed +0.2mV. The findings indicated that for SP-130, preferential adsorption may be present. For the slurry with limestone 2, SP-130 preferentially adsorb onto cement particles, resulting in a zeta potential which is more similar to that of the pure cement slurry. On the other hand, due to the highly positive surface of natural sand, competitive adsorption of SP-130 between cement and natural sand was possible. In actual fact, due to the more negative zeta potential present, it could be postulated that natural sand in this case may have a higher affinity for the plasticizer than cement. This is more pronounced due to the fact that more cement is present in the system than natural sand. However, this is only valid based on the assumption that orientation of incoming polymers to the surfaces of each particle is independent. It should also be noted at this point that in the cement/filler slurry, constant release of ions from the dissolution of cement is present. However, the amount of cement present is less than in a pure cement system, thus effect may be less to the point of it being less effective in forming double layer, especially in the situation of competitive adsorption of cations by fillers.

Another point to note is the stability of the particles in solution. In general, samples suspended with MapaPlast displayed larger zeta potential values than that with SP-130. This indicated a lower tendency for flocculation of the particles in the former, resulting in a seemingly better dispersion.

Looking at slurry systems with added MapaPlast, it can be observed that stability of both natural sand and limestone 2 systems should be similar due to the similar zeta potentials, whereas that with SP-130 differed. However, it is important to take into account the steric effect exerted by the polycarboxylate based polymer in SP-130, which can greatly alter the dispersion and reduce flocculation in a system which appear to have low stability by zeta potential measurements. Additionally, in limestone 2, the fact that SP-130 may preferentially adsorb onto cement particles can further increase the overall dispersity of the system.

For all samples measured, the zeta potentials were relatively stable after the initial few minutes. Little changes were observed for measurements up to 10min. This indicated that firstly overall variation of fillers surfaces is minimal after the initial change, and secondly adsorption of the plasticizers on the particle surfaces is rapid and stable as long as no external factors are added to influence this attraction.

3.2 Area 2

This area focuses on the zeta potential of three fillers and the effect of adding a plasticizer, SXN as a function of time. SXN is a polycarboxylate based superplasticizer, made up of two different types of copolymers with varying side chain lengths and grafting densities.

3.2.1 Zeta potential of fillers in cement pore solution

Three different fillers were suspended in standard FA cement pore solution and the zeta potentials with and without SXN were measured. The three slurries prepared were static systems and thus ions from pore solutions were not replenished after being consumed by fillers.

All three fillers possessed very different zeta potential values (**Figure 7**). Quartzite is negative at a zeta potential value of -3.4mV due to the innate Si-O$^-$ surfaces arising from the quartz ions. Limestone 1 lies on the isoelectric point and possesses a zeta potential value of 0.0mV. This renders it neutral and increases its tendency to flocculate. Additionally, it may be less susceptible to interactions with incoming ions. However, it should be noted that this is the net overall zeta potential of the heterogeneous particles, thus variation in charges along the surfaces of the fillers is to be expected. Another noticeable point is the variation in zeta potential between limestone 1 (0 mV) and limestone 2 (-2.9 mV). Despite being both limestones, differences in the innate zeta potential exist. This difference in the zeta potentials can be attributed to many factors including the type of cement pore solution employed, particle size of the limestone samples and also the inherent surface charge of the particles. As a result, it is important to note that when quantifying the zeta potentials of systems, differences conditions including different materials of the same generic could lead to drastic variation in the values. Anorthosite was measured last and it showed a very positive surface by registering a zeta potential of +12.4mV. The high zeta potential values of anorthosite makes it the most stable filler among these three which are compared here.
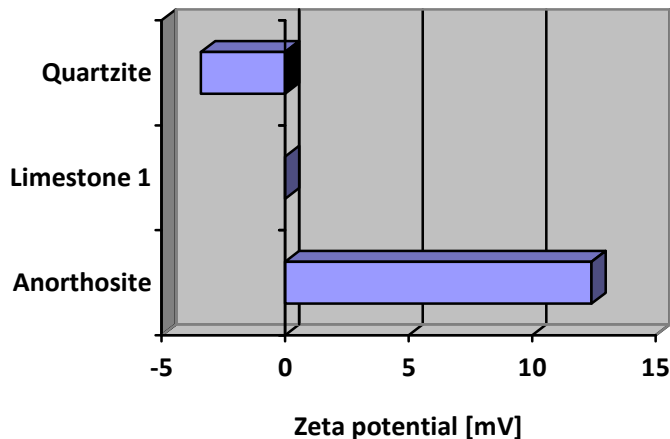
Figure 7 Zeta potential of the three fillers in cement pore solutions prepared at w/c of 0.5

The differences in zeta potential of the fillers render them to interact very differently with superplasticizers in solution, which will be discussed in the next section. The zeta potential of each filler slurry was measured as a function of time for up to 1h and it was found that little change was observed. This indicated that surfaces of the filler particles interact and is saturated with the ions from the cement pore solution very rapidly. Additionally, the fillers are stable and the surfaces do not alter much when particles are left suspended in the harsh environment of cement pore solution.

3.2.2 Effect of SXN addition (similar to delayed addition)

SXN superplasticizer was titrated into the filler slurry at a constant rate of 0.2ml per dose till a total amount of 10ml SXN was added to the slurry. The final added amount of SXN was 19% by weight of filler (bwo filler), partially due to the high w/fi content of this system. When cement is used as a comparison, the %bwoc of the maximum amount of SXN added is <2.5% for all filler systems, rendering them to fall in good order of the usual dosage of superplasticizers added in a normal concrete application. **Figure 8** displays the variation in zeta potential of the three fillers as a function of SXN addition (%bwo filler) whereas **Figure 9** gives a relative idea of the amount of SXN added when cement is present. The dosage in **Figure 9** is calculated based on the assumed amount of cement present arising from the w/c.
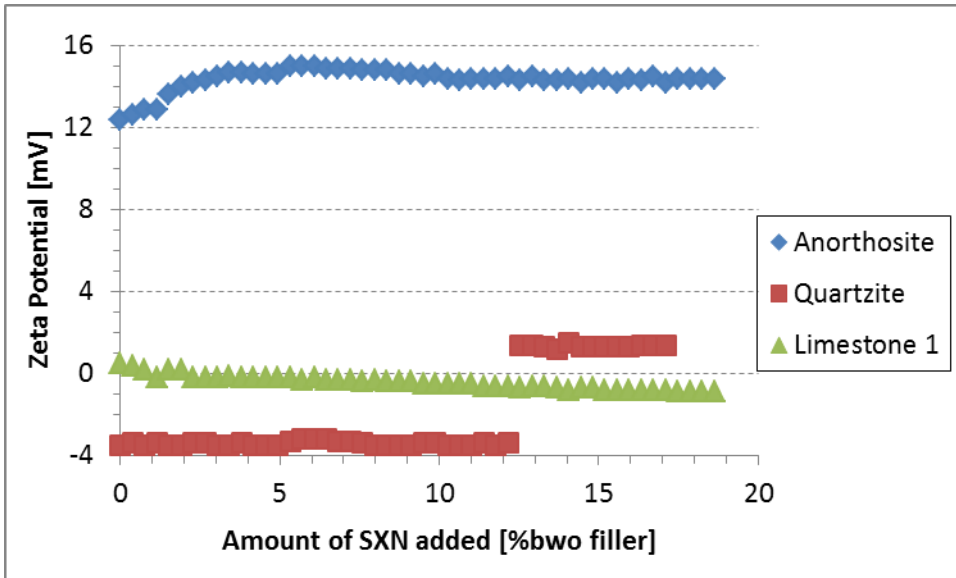
Figure 8 Zeta potentials of three fillers slurries as a function of added amount of SXN as a function of filler (w/c = 0.5)
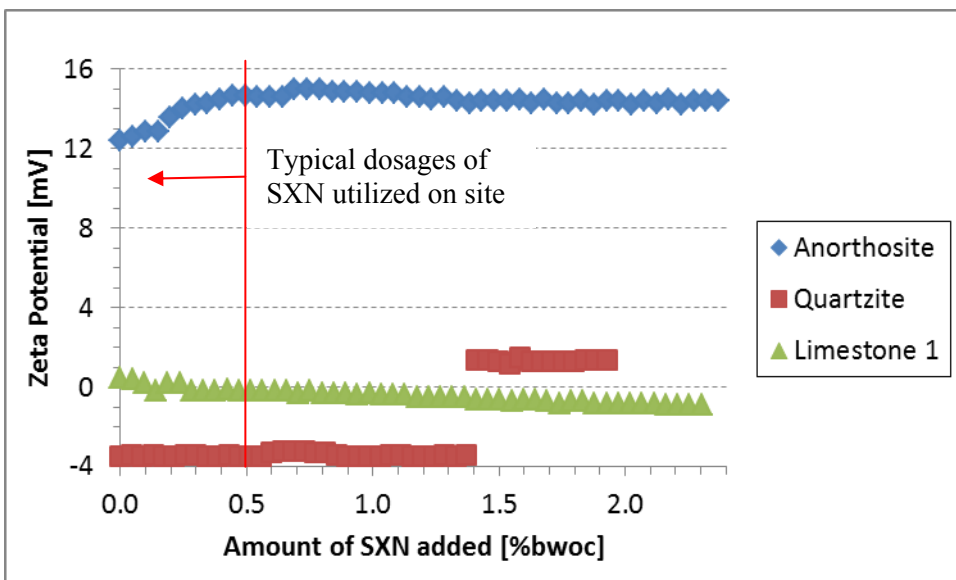
Figure 9 Zeta potentials of the three fillers slurries as a function of added amount of SXN by weight of cement (w/c = 0.5). Dosages less than red line marks the typical dosage of SXN employed on site for dispersion cements. Red line indicates approximate maximum amounts of SXN normally dosed during actual application

As expected, the zeta potentials of the three different fillers in the presence of SXN are very different. The variation was dependent on the innate zeta potential of the fillers, whereby in the presence of increasing amount of SXN, the zeta potential of anorthosite remained positive, limestone 1 around zero with a slight downwards trend and quartzite negative, which finally increasing to be positive at a SXN dosage of ~12.5%bwo filler (or 1.4%bwoc). These differences can be explained by the differences in the surfaces of the fillers, and the nature of SXN plasticizer.

SXN superplasticizer is a commercial product made up of two polycarboxylates based polymers; one with long side chains and the other short. As a result, selective adsorption of the polymers can occur, resulting in the preferential adsorption of one polymer over the other. When polycarboxylate based superplasticizers are adsorbed onto the surfaces, these polymers will exert a steric effect on the surfaces of fillers after adsorption. On the other hand, when more anionic polycarboxylates with shorter side chains are adsorbed, a general decrease in zeta potential might be possible. Additionally, due to the high w/fi, the amount of electrolytes present in the cement pore solution may be present in excess to exert an effect for double layer formation.

Looking at the filler slurries specifically now, in the anorthosite filler slurry, the sample registered an increase in zeta potential from 12.4mV to 15.0mV when SXN was titrated to the sample. The highly positive surface of anorthosite particles render them ideal docking sites for incoming polycarboxylate based plasticizers, regardless of charge density. In such a situation, the adsorption can be both electrostatic and thermodynamically driven. The change in zeta potential signified that adsorption of SXN on the filler surface occurred and the saturation adsorbed amount of SXN on the surface of anorthosite particles was achieved at around 0.5%bwoc. Further increase in SXN dosage did not present any further adsorption significantly. This lack of further adsorption entails an increase in free polymer in solution, which may aid in the dispersion of particles in solution [4]. The increase in zeta potential when SXN was added could be due to the double layer formation where some cations may adsorb onto the surfaces of the polymers. However, due to the limit amount of cations in solution, steric effect exerted from the long side chains of polycarboxylate based polymers and even the repulsive effect arising from the distance between anorthosite surfaces and the incoming cations, the increase in zeta potential is not significant.

In the case of limestone particles, titration of SXN to the slurry registered a decrease in zeta potential as a function of dosage, even up to the maximum dosage added. This implied that limestone has a low affinity for the SXN plasticizers, thus no saturation was achieved in the course of this experiment. Additionally, as indicated by the gradual decrease in zeta potential, the preferred polymer for adsorption onto the limestone surfaces is the more anionic polymer possessing shorter side chains. The lack of significant change in the zeta potential during the titration of SXN could arise as a result of reversible binding of cations from solution onto the polymers.

Lastly, the adsorption of SXN onto quartzite was analysed. The zeta potential of the quartzite slurry remained relatively constant till an added SXN dosage of 1.4%bwoc, whereby zeta potential increased from -3.4mV to +1.5mV. The constant zeta potential of the quartzite slurry with increasing amount of SXN could indicate that amount of SXN adsorbed onto the surface was very low and a threshold amount of SXN was needed for any significant effect to be seen on zeta potential measurements. In this case, 1.4%bwoc of SXN was the minimum dosage. At this point, sufficient polymers were adsorbed and a reversal of charge by the formation of double layer was thus registered.

It should be noted that adsorption of both type of polycarboxylate based polymers by the fillers occur in all cases, but they vary according to the preference for adsorption or to exist as non-adsorbed polymers in solution. In general, when polymers possessing long side

chains are present, they can exert a steric effect with similar adsorbed polymers on the surfaces of particles, thus improving the overall dispersion of the system. On the other hand, more anionic polymers with shorter side chains possess less of such trilogy effect.

Looking from a more practical point of view, SXN is generally dosed into concrete applications at a concentration of no greater than 0.5%bwoc (**Figure 9**). According to zeta potential measurements, it can thus be concluded that the variation in the adsorption and thus dispersing effect of SXN on these three fillers would be very different. In the case of anorthosite, increasing SXN addition till 0.5%bwoc would show an increase adsorbed amount of polymers, whereas for limestone, the variation in adsorbed amount is much less than that for anorthosite. Variation in that with quartzite is more unpredictable, but generally, any physiochemical observations is independent from the influence of charge.

For more certain evaluation of the results, adsorption studies e.g. via total organic carbon (TOC) measurements or gel permeation chromatography (GPC) should be performed. The advantage of GPC over TOC is that molecular weight dependency of adsorbed polymers could be determined by the latter method. Additionally, macroscopic dispersion studies such as rheology or mini slump tests should be performed complementary to the mentioned tests for a better overview on the dispersing effect of SXN on fillers, etc.

Conclusion

The zeta potentials of five different fillers and three commercial plasticizers were explored in this report. The main purpose was to determine how these materials interact with each other to aid dispersions, in an effort to explain the macroscopic observations of sedimentations and interactions of fines in crushed aggregates with plasticizers. Generally, it was found that all fillers possess an inherent zeta potential which can undergo charge reversal upon addition into the cement pore solution. This can be attributed to the high electrolyte content of the pore solution, allowing surface adsorption of the ions from solution by electrostatic attraction. In turn, this new surface on the particles acts as a docking site for incoming plasticizers. Upon adsorption of plasticizers, the plasticizers disperse the particles either by electrostatic attraction (shown distinctively by zeta potential values) or steric hindrance (a net effect of zeta potential and hydrophobic repulsion effect) in solution.

Of interest, in a filler/cement slurry which was analysed in **Area 1**, these two materials can undergo competitive adsorption of the plasticizers, dependent on the type of filler or plasticizer present. In this study, natural sand competed with the standard cement for incoming polymers, whereas preferential adsorption occurred on the cement surfaces as compared to limestone 2, especially when SP-130 was present, arising from the charge affinity of the surfaces to polymers in solution.

In **Area 2**, the zeta potentials of the three fines differed greatly which accounted for their differences in interactions with SXN. Most importantly, the stability of SXN with anorthosite was observed to be the highest, whereby saturation occurred at a dosage of 0.5%bwoc, whereas uptake of SXN by limestone 1 was a gradual process. In the case of quartzite, the results were less predictable from mere zeta potential analysis.

Indeed, this report here showed that fillers interact with plasticizers. It is thus important to look at their interactions and not assume that they are inert especially where more and more applications such as SCC and usage of more crushed aggregates are present.

Additionally, zeta potential measurements can describe the dispersing nature, adsorption profiles of plasticizers and also flocculation effects. However, certain degrees of uncertainties are present when this method is employed as a stand-alone in the determination of mechanistic theories. Therefore, as an outlook, it is thus proposed that further investigations on e.g. adsorption studies by total organic carbon (TOC) analysis or gel permeation chromatography (GPC) to be conducted. Additionally, a proper correlation between colloidal chemistry and dispersion effects, both micro and macroscopically through test methods such as electron microscopy with slides imaging and 'mini slump' test etc are to be performed as a bridge between effects occurring at the nanoscale and the macroscopic observations such as sedimentation.

References

J. Plank, C. Hirsch, Impact of zeta potential of early cement hydration phases on superplasticizer adsorption Cement Concrete Res 37 (2007) 537–542.

Lange A., Hirata T., Plank J., The role of Non-adsorbed PCE molecules in cement dispersion: Experimental evidence for a New dispersion mechanism, in V. M. Malhotra (Ed.) 10th CANMET/ACI Conference on Superplasticizers and Other Chemical Admixtures in Concrete (Proceedings) ACI Prague (2012) SP288.30. pp. 435–449.

Peng Y., Sedimentation and Bleeding of Cement Paste, Doctoral Thesis, Doktoravhandlinger ved NTNU, ISSN 1503-8181 (2014) 89.

Rhodes M., Introduction to Particle Technology, 2nd Ed. John Wiley &Sons, Ltd, UK, ISBN 978-0-470-01428-8 (2008) 450p.

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