SINTEF Building and Infrastructure   Serina Ng and Harald Justnes

Rheology of blended cements with superplasticizers

COIN Project report 58 – 2015

SINTEF Building and Infrastructure

Serina Ng and Harald Justnes

Rheology of blended cements with superplasticizers

FA: Environmentally friendly concrete structures

SP 1.1 Binders with low emission and reduced resource consumption

COIN Project report 58 – 2015

Cooperation partners / Consortium Concrete Innovation Centre (COIN)

Kværner Engineering
Contact: Jan-Diederik Advocaat
Email: Jan-Diederik.Advocaat@kvaerner.com
Tel: +47 67595050

Saint Gobain Weber
Contact: Geir Norden
Email: geir.norden@saint-gobain.com
Tel: +47 22887700

Norcem AS
Contact: Terje Rønning
Email: terje.ronning@norcem.no
Tel: +47 35572000

NTNU
Contact: Terje Kanstad
Email: terje.kanstad@ntnu.no
Tel: +47 73594700

Mapei AS
Contact: Trond Hagerud
Email: trond.hagerud@mapei.no
Tel: +47 69972000

SINTEF Building and Infrastructure
Contact: Tor Arne Hammer
Email: tor.hammer@sintef.no
Tel: +47 73596856

Skanska Norge AS
Contact: Sverre Smeplass
Email: sverre.smeplass@skanska.no
Tel: +47 40013660

Norwegian Public Roads Administration
Contact: Kjersti K. Dunham
Email: kjersti.kvalheim.dunham@vegvesen.no
Tel: +47 22073940

Unicon AS
Contact: Stein Tosterud
Email: stto@unicon.no
Tel: +47 22309035

Veidekke Entreprenør ASA
Contact: Christine Hauck
Email: christine.hauck@veidekke.no
Tel: +47 21055000

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

With the drive towards a greener construction industry, focus has been placed on minimizing the emission of CO_2 from cement clinker production. This led to an increase in the utilization of blended cements in the construction industry. Currently, it is common practice to replace up to ~20 % of the cement clinker with supplementary cementitious materials to reduce the amount of CO_2 emission. However, the aim is to further increase this substitution to further improve the environmental situation. As a result, more research and a better understanding of their effective performance are required. One such aspect where additional studies are required for such materials is in their interactions with different admixtures, especially at higher addition of the supplementary cementitious materials. Therefore, the purpose of this investigation is to study the rheological impact of different superplasticizers, commonly employed in conventional ordinary Portland cement systems on a selection of blended cements.

For investigation purposes, five different superplasticizers across the whole range were selected; a lignosulfonate, a naphthalene based polycondensate and three different polycarboxylates with varying side chain lengths and charge densities. They were initially dosed according to commercial usage (0.2 % by weight of cement) to reflect the practicality of these polymers in the blended cements as compared to that conventionally employed.

As supplementary cementitious materials, calcined marl and fly ash were chosen and utilized at replacement percentages of 20, 40 and 60 wt.% respectively. A low w/c ratio of 0.36 was selected to prevent bleeding and segregation of the cement pastes, particularly in the case of fly ash loaded systems. In situations where little flow was observed, much higher dosages of the superplasticizers were employed (up to 0.8 %by weight of cement).

Method wise, the rheological properties of the cement pastes were measured quantitatively by a Physica MCR 300 rheometer to ensure. Such a measurement method is generally favored over manual measurements such as the mini slump test, etc as it can give accurately a concise and pinpoint measurement independent of the user. The heat released up to 24 h was measured by the TAM air isothermal calorimeter, while the packing density and water demand of the cement pastes were analyzed employing centrifugal consolidation subjected to a compaction energy of 4,000 rpm for a period of 5 min.

The main findings in this work are as follow:

Generally, the blended cements showed similar trends in their interactions with superplasticizers as the ordinary Portland cement. The polycarboxylate based superplasticizers (NRG, SX and SPN) were more efficient in dispersing all cement systems than the naphthalene based (NAPh) and lignosulfonate (LS). Additionally, the lignosulfonate superplasticizer increased the flow resistance of the cement pastes (decrease fluidity of the paste) with increasing dosages.

In the fly ash systems, an increase in fly ash content in the cement resulted in an increase in fluidity of the neat cement paste. No bleeding was detected even when up to 60 wt.% replacement of cement clinker by fly ash was performed. The fly ash particles were relatively inert and acted as fillers. Minimal dissolution of fly ash particles occur in the paste and this is relatively negligible as compared to the bulk reaction of the cement clinkers during early age. Upon addition of superplasticizers, the trend in performance of the superplasticizers mimicked that of an ordinary

Portland cement and the plasticizing effectiveness was as follow: NRG > SX > SRN > NAPH > LS. On the other hand, the slump flow retention (ability of maintaining flow resistance over time) was SRN > SX > NRG > LS ≈ NAPh. Fly ash particles interacted with the superplasticizers. However, the impact on the interaction with clinker phases was low and any adsorption was reversible. NRG proved to be a very good plasticizer, where no rheological data could be measured in a cement containing 60 wt.% fly ash when 0.2 %bwob of this polymer was added due to segregation of the paste.

Comparing a fly ash cement (pre-blend in the cement mill while grinding) and a manually blended cement each containing ~20 wt.% fly ash, the flow resistance of the neat cement pastes were totally different. The manually blended cements displayed a better much better flow than the former, which possessed rheological properties similar to that of an ordinary Portland cement. This difference can be attributed to the availability of effective surface area from the fly ash which was exposed to undergo interaction with superplasticizers or water molecules in presence of clinker phases.

In the calcined marl systems, the calcined marl was shown to be a strong adsorber of water. The affinity or the water retaining capacity of the calcined marl per unit mass decreased as the solid replacement percentage increase in presence of a constant amount of water (w/c = 0.36). In general, an increased replacement of cement clinker with calcined marl resulted in a decrease in flow of the neat cement pastes and the paste stopped flowing when 60 wt.% calcined marl was utilized. Upon addition of superplasticizers, calcined marl competed with the cement clinkers for superplasticizers. The extent of competition was masked by the uptake of water and also varied according to the characteristic of the superplasticizers. SX, possessing an intermediate side chain length and charge density proved to be a much better dispersing agent here. The plasticizing effectiveness of the superplasticizers was SX > NRG > SRN > NAPh > LS, similar to an ordinary Portland cement or in the case of cement containing fly ash with the exception of SX polymer. The effectiveness of the dispersing agents on slump retention was SRN ≈ SX > NRG > LS > NAPh.

In the investigation of heat released during hydration of cements, pure fly ash showed negligible amount of heat released up to 24h. In cements containing fly ash, the hydration of the cements was retarded with increasing fly ash content, confirming the dilution effect of fly ash on the system. The effect of superplasticizers (degree of retardation and change in total heat released) was similar to that observed in an ordinary Portland cement. Pre-blended fly ash cement displayed similar hydration profile as the ordinary Portland cement since it has been finer ground (Blaine 454 vs. 382 m^2/kg) to compensate for the sluggish reaction of FA

Pure calcined marl, on the other hand, displayed thrice the amount of heat released as that for a pure fly ash sample. This, in comparison to the heat evolved in cement hydration was however, negligible. When blended with cement, the calcined marl contributed to the hydration of the cement paste. In the case of calcined marl addition, no retardation was observed, up to a loading of 40 wt.% calcined marl. However, a replacement by 60 wt.% calcined marl displayed a change in hydration profile, indicating that hydration of calcined marl dominated at higher replacement percentages. Superplasticizers only affect and retard the hydration of the cement pastes at threshold superplasticizer dosages of 0.4 %by weight of cement.

Table of contents

1   Introduction

1.1   Principal objectives and scope

The aim of this report is to investigate the rheological properties of blended cement pastes with addition of different superplasticizers, where two different supplementary cementitious materials and five superplasticizers were employed. In all, the effect of the variation in type and dosage of the superplasticizers on the different type and degree of substitution of the cement by supplementary cementitious materials was investigated here.

The two inorganic materials involved firstly a fly ash sample, obtained from Norcem AS. This fly ash is commonly used in their cement production. Three different concentrations of fly ash were used in the substitution of cement clinkers, namely 20, 40 and 60 wt.% respectively. A commercial fly ash cement containing 18.2 wt.% fly ash was also investigated as a comparison between cement samples with fly ash prepared by simple mixing and when mixing was performed already in the cement mill during grinding. The second inorganic material was a calcined marl, prepared at 850 °C. Likewise, three different amounts of calcined marl was employed; 20, 40 and 60 wt.% substitution of the cement clinker. These, coupled with a standard ordinary Portland cement gave a total of 8 binder materials for testing.

For the superplasticizers, three of them are based on polycarboxylate chemistry, while the other two were a naphthalene sulfonate, and the other was a pure lignosulfonate. The main dosage employed for all binder systems was 0.2 %bwob, based on the pure polymer amount. Other dosages of 0.1, 0.4 and 0.8 % bwoc of superplasticizers were employed according to the type of binder utilised to investigate the effect of the amount of superplasticizers added on the rheological properties.

Rheological analysis was performed employing the principles of a parallel plate rheometer, while the packing density and water demand were followed by the centrifugal consolidation method. Lastly, the impact of varying systems on the heat of hydration of the cement slurries was investigated by isothermal calorimetry and a correlation between this heat evolution profile and the rheological properties of the cement pastes was search for.

1.2   Background

The building sector is one of the most dominating industries globally due to the constant and growing demand of new construction materials in respond to the needs in the infrastructure business. Statistically, production of concrete is the second largest by volume [1, 2] and it accounts for a large part of our economic and environmental impact. Among the materials in a concrete, the cement is globally produced, achieving a value of ~3.5 billion tons in 2011 [3, 4]. Generally, production of one ton of Portland cement clinker emits an equivalence of about one ton of CO_2 if pulverized coal is used as a fuel, depending on the technology employed in the cement kiln. This massive amount of cement produced worldwide resulted in ~ 6% CO_2 emission annually, making the cement industry the third largest CO_2 emitter after housing and transport [5, 6].

In an effort to reduce this, a drive towards greener and more environmentally friendly binder systems is the general objective of politics all around the world. The aim is to reduce this level of CO_2 emissions to ~ 50% by 2050 as stated by the World Business Council for Sustainable Development. The two main approaches are technological improvements such as implementation of co-processing and usage of alternative fuels in cement kilns, while the second involves the production of new cement binders involving the replacement of cement clinkers with supplementary cementitious materials (SCMs) to achieve cements containing less clinker contents. Generally, the latter method is more direct and immediate as

technological changes in the cement kilns usually require an overhaul modernization of the existing equipment, which often is time consuming and comes at a very high price. In the second method, new cements are produced by blending the cement clinkers with SCMs which are known to not affect but also maintain the binding properties of the cement products. Many natural, as well as synthetic SCMs can be utilized as suitable materials and these include industrial by-products such as granulated blast furnace slag (GBFS) from the steel industry or fly ash from coal power plants, whereas natural pozzolanic materials include clays, particularly after calcination. The advantage of such blended cement is a direct reduction in CO_2 emission, which is reflected in the percentage of substitution by the SCM materials, making them a popular choice in the cement industry. However, incorporation of the SCMs general results in a change in the working properties of these binder materials and thus compatibility with other additions could be potential challenges.

One parameter which is commonly affected by the introduction of SCMs in blended cement is rheology. The rheology of concrete and cement is commonly altered and improved by the addition of admixtures such as superplasticizers, retarders, etc. The introduction of admixtures improves not only the user friendliness of cementitious materials on site, but also increase and enable enhanced final properties and aesthetic of the composite or buildings. Significantly, the ease of working with concrete possessing improved rheoloigcal properties has created millions of savings and earnings, and optimization of labour forces for the construction industry. This demand of materials possessing ideal workability is expected to continue and grow with the rising usage of construction materials, such as in the area of household applications, where increase demands for do-it-yourself formulations appears on the market.

The largest group of rheology regulators among the admixtures consists of superplasticizers which act by inducing dispersing effect in the early ages of cement. These superplasticizers consist of a wide variety of chemicals, ranging from salts of carboxylic acids and modified lignosulfonates (natural products) to the naphthalene- and melamine- based polycondensates, and finally the largest group of polycarboxylates derivatives possessing a large extent of different functionalities. With normal Portland cements, extensive research has been performed on these admixtures, both in determining their behaviors and effectiveness on rheology, and also the improvement of their additions on the final strengths and mechanical properties of concretes. The mechanisms underlying the effective dispersion of OPC by these admixtures as driven by electrostatic repulsion or steric effects have also been widely discussed. Their effectiveness is generally accounted for by the attributes of the clinker and hydrate phases [7, 8], and the specific characteristics (both structural and chemical) of the admixtures added [9, 10].

With the utilization of blended cement, a different rheological behaviour arising from the variation in interaction between the admixtures and cement particles can be expected. The basis of superplasticizers in OPC based systems has been attempted to be applied as mechanistic assumptions in the studies of blended cements previously. However, with the deviation in chemical compositions of the blended cements from OPCs, differences in their interaction including colloidal chemistry, etc are possible and can generate many controversies in the direct application of this understanding. Some researches on the fundamentals of the colloidal interface of the polymer-inorganic materials have been performed in both isolated SCM systems [11, 12] and selected blended cement systems [13]. Despite the extensive studies, more importantly, an actual understanding in the applied rheological effectiveness of these superplasticizers is required to ensure optimal usage of the admixtures in such system. Additionally, the influence of these admixtures on blended cements possessing higher replacement amounts of SCMs with the drive in creating a greener construction industry is also to be expected.

2   Experimental

2.1   Materials

An ordinary Portland cement (OPC), a standard fly ash cement (faC), a fly ash (FA) and a calcined marl (cM, calcined at 850 °C) were employed in this investigation. The main difference between these two cements lies in the presence or absence of 18.2 wt. % fly ash as well as the higher specific surface of faC. The two cements and fly ash were supplied by Norcem A.S. Brevik, Norway, while the calcined marl was from Saint-Gobain Weber. Table 1 displays the chemical compositions of the cements, fly ash and calcined marl respectively. The calcined marl contains mainly smectite (>50%) and calcite (~25%). Minor amounts of kaolinite (~8%), quartz (~4%), siderite (~3%) and pyrite (~1%) are present. The specific Blaine surfaces of the ordinary Portland cement, fly ash cement and fly ash are 382, 454 and 357 m^2/kg respectively. In the case of calcined marl, the specific surface area as measured by BET was 15.1 m^2/g. However, Blaine and BET can not be compared directly as Blaine being based on air flowing through a pack of powder is related to the "outer" surface of particles (i.e. voids between them), BET measures both outer and inner surface of non-connected pores and cracks.

Table 1. Chemical Compositions of standard cement, blended cement and fly ash

	Portland cement	Blended cement	Fly ash	Calcined marl
SiO_2	20.8	26.9	50.0	49.6
Al_2O_3	4.6	8.1	23.9	18.1
Fe_2O_3	3.5	4.2	6.0	10.6
CaO	61.6	51.5	6.3	14.1
MgO	2.4	2.2	2.1	2.9
P_2O_5	0.2	0.2	1.1	0.2
K_2O	1.0	1.0	1.4	2.4
Na_2O	0.5	0.6	0.6	0.7
SO_3	3.5	3.2	0.4	-
Alkali	1.1	1.2	1.6	-
Total	99.2	99.1	93.4	98.6

For dispersions, a total of five commerical superplasticizers were utilized, namely Mighty 150, Ultrazine NA, Dynamon NRG-700, Dynamon SX-130 and Dynamon SRN respectively. Mighty 150 is a polynaphthalene sulfonate based superplasticizer supplied from Sika Norge A.S. and usually has a solid content of 40 ± 0.5 %. Ultrazine NA is supplied from Borregaard A.S. and is a purified sodium lignosulphonate with a high molecule weight. It is general sugar free (or very low in sugar content) and contains very low organic acid. Dynamon SX-130, Dynamon NRG-700 and Dynamon SR-N are polycarboxylate based superplasticizers and supplied from Mapei Escon A.S. Among the polycarboxylate samples, Dynamon SX-130 is commonly employed in ready-mix systems and has intermediate side chain lengths and charge density along its backbone. Dynamon NRG-700 is commonly used in the element industry and gives the shortest workability. However, due to the high backbone charge density and longer side chain lengths, it has the highest plasticizing effect amount the 3 polycarboxylates. Dynamon SR-N possesses intermediate workability and plasticizing effect due to its lower charge density and side chain lengths. For simplicity, the superplasticizers will be denoted as follow in the report: Mighty 150 (NAPh), Ultrazine NA (LS), Dynamon NRG-700 (NRG), Dynamon SX-130 (SX) and Dynamon SR-N (SRN).

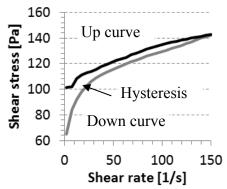All materials were utilised as per obtained. For preparation of blended systems, the OPC and fly ash/ calcined marl were mixed manually in the ratio of 4:1, 3:2 and 2:3 respectively. Therefore, a total of eight cementitious systems: OPC, faC, 20% FA/OPC, 40% FA/OPC, 60% FA/OPC, 20% cM/OPC, 40% cM/OPC and 60% cM/OPC were studied. For the polymer samples, all samples were prepared as solution possessing a solid content between
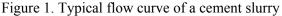
20 to 30 wt.% for ease of dosing. 4 different polymer dosages were employed: 0.1, 0.2, 0.4 and 0.8 %bwob respectively.

2.2   Experimental Procedures

The cement slurries were prepared by adding the dry powder mix to the water at a w/c ratio of 0.36 over a period of 0.5 min. This low w/c ratio of 0.36 was chosen to emphasize on the workability of superplasticizers in the two different systems employed here: cement with fly ash or calcined marl respectively. For cements with added fly ash, the low w/c ratio was ideal to prevent excessive segregation. In the case of calcined marl, the usage of higher dosages of superplasticizers was performed to achieve the desired flow. The superplasticizer at the appropriate dosage was added to the water and homogenized beforehand. After 0.5 min, the mixture was blended at high shear rate for 1 min, let stand for 5 min, followed by a final high shear mixing of 1 min to avoid false set. High shear mixing was performed utilizing a mixer with a power of 500 W and maximum capacity of 200 mL to ensure well dispersed cement slurries exposed to high shear energy as in a concrete. In each mix, the amount of slurry prepared was ~ 205 g to minimise weighing errors. The obtained slurries were subsequent employed in the rheological, calorimetric and packing density analyses.

For rheological measurements, ~ 2 g of the prepared slurries were employed here. All measurements on the samples were started within the first 12 minutes after first contact of dry powder with water. A Physica MCR 300 rheometer (Anton Paar, Graz/Austria) equipped with a parallel plate geometry was utilised. Measurements were conducted at 20 °C and the up and down flow curves was measured over the range of shear rates from 2 to 150 s^{-1} over a period of 6 min after an initial homogenisation of 1 min at a shear rate of 100 s^{-1}. During analysis, samples were only measured when the initial force exerted by the parallel plates on the sample was less than 50 kN. Measurement of up/down flow curves is to check the degree of hysteresis caused by agglomeration. The down flow curve is fitted with two linear regression at the high and low shear rates (threshold limits of <20 and >50 s^{-1} respectively).The Bingham viscosity (μ_1 and μ_2) can be obtained from the gradient of these two fits (low and high shear rates respectively), while the dynamic yield point (τ_d) of the cement slurry is determined from the y intercept of the second linear regression line obtained at high shear rate (> 50 s^{-1}). The flow resistance (FR$_2$) which is a measurement of the work done to shear the paste within the given range of shear rate is calculated from the area under the down curve (Figure 1, left). The static yield point (τ_{10}) as determined by the amount of shear stress needed to produce a shear rate of 0.1 s^{-1} after rest of 10 sec and 10 min were measured up to a maximum shear stress of 500 and 750 Pa respectively, and measurements were set to end and jump to next test segment when dQ/dt > 10. This experimental sequence was repeated four times to give a profile of the variation in rheological properties of the cement pastes as a function of time. A rest period of 12.5 min is introduced between each test period, giving total test duration of ~ 1.5 h (22.5 min/cycle). The flow resistant versus time evolution was used as a measure of "slump retention" (i.e. retained when insignificant change).

Figure 1. Typical flow curve of a cement slurry

Calorimetric analysis was performed for the first 24 hours of cement hydration. ~8g of cement slurry prepared was added into a glass vial, sealed with a lid and placed in the isothermal TAM Air calorimeter (TA Instrument, New Castle/USA). Measurements were performed against a calibrated reference of inert alumina powder of similar mass. The time of placement was recorded and all subsequent hydration profiles are calculated after 1 h due to the excess heat transfer from preparation during the first hour of cement hydration.

 The packing density and water demand of the cement slurries was determined by a modification of the centrifugal consolidation method, proposed by Miller [1]. ~80 g of cement slurry was added into a 50 mL falcon tube and subjected to centrifugation at 4,000 rpm for 5 minutes. The supernatant was removed with a pipette and the weights of the cement sample (before and after compaction/removal of liquid) were determined. The packing density of the cement slurry was calculated as a ratio of the volume of cement to the total volume of cement and water present in the residue after centrifugation. Assuming that only water was extracted during the centrifugal process, the water demand and packing density at this applied compaction energy can thus be determined.

3   Results and discussion

This chapter will be divided into four sections mainly based on the type of supplementary cementitious materials employed in the blended cements. The first section describes the rheological and hydration profile of the ordinary Portland cement utilized in this investigation, and both the addition and absence of superplasticizers will be discussed. This is followed by the next two sections where the rheological influence of superplasticizers on blended systems, will be highlighted. The first consists of the discussion on the fly ash blended cements, where a comparison between commercially blended cement and manually mixed system will be described. While the latter involved the rheology of calcined marl/OPC blended systems. A comparison of the heat released profile through calorimetry analysis of all the systems will be finally given in the fourth section.

3.1   Influence of superplasticizers on ordinary Portland cement

3.1.1 Neat ordinary Portland cement (OPC)

The hydration of the neat ordinary Portland cement paste was first investigated and its rheological behavior as a function of time can be observed in Table 2. In general, when the cement hydrated, the slurry thickened and reached its setting point. Here, continuous shearing was performed on the cement paste, thus the rheological results observed were a combination of the normal hydration and crystal growth of the cement paste and the shearing process which deglomerated the hydrate particles formed in situ. In each cycle, the μ_1/μ_2 possessed a value greater than 1, indicating shear thinning of the cement slurry as immediate deglomeration outweigh the impact from crystal growth of the particles in the matrix during hydration. The initial viscosity μ_1 which was characteristic of the apparent viscosity of the cement slurry subjected to shear stress from rest, decreased with each cycle. This signified that hydration of the cement particles, thus agglomeration of the paste occurred faster at the onset of hydration, which slow down gradually. On the other hand, the increase in μ_2 confirmed that the cement paste thickened with time despite the shear thinning effect from the rotation of the rheometer plates.

Table 2. Rheological properties of the neat OPC slurry as a function of time, w/c = 0.36

	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
RUN 1	4.06	0.28	14	230	105	255	150	35,400	790
RUN 2	4.35	0.32	13	280	110	255	145	42,000	3,950
RUN 3	3.63	0.99	4	160	95	420	325	31,200	-15,540
RUN 4	1.25	0.60	2	60	20	110	90	15,100	8,340

$\mu_{1, 2}$:   Shear viscosity of up and down curves resp.
$\tau_{d, s10s, s10m}$:   Dynamic and static yield points at 10 s and 10 min resp.
marked in red: τ_s registered when dQ/dt > 10

The dynamic and static yield points presented an indication of the amount of force needed to shear the cement slurry. A general decrease in yield stress was observed for this cement slurry. However, a sudden increase in the τ_{10m} in run 3 and the rapid drop in subsequent yield stress indicated that the cement paste may have undergone excessive thickening, resulting in a disruption of proper shear measurement. This was confirmed by the rapid drop in the flow resistance (FR_2) and hysteresis of the cement slurry in run 3 (Figure 2). It should be noted that the $\tau_{s\ 10m}$ values measured in run 3 and 4 were not true shear stress values as the measurements were interrupted when dQ/dt was greater than 10.

From this investigation, it can be concluded that care must be taken when the FR_2 of a system exceed 40,000 NM/m³s as excessive thickening of the cement slurry may have occurred, rendering the data observed to be unreliable. Secondly, τ_d is an ideal indication of

the rheological state of the cement slurry, followed by FR_2 and potentially μ_2, but only when the shear limit is not reached.

Figure 2. Inaccurate measurement of shear stress due to excessive shear stress exerted by cement paste at run 3, w/c = 0.36

Figure 3 displays the heat of hydration curve for the neat ordinary Portland cement slurry. As observed, the rate of heat evolved through the hydration of this cement reached a maximum power of 0.22 mW/g at 5.6h, a second maximum of 0.21 mW/g at 8h and a third peak of 0.20 mW/g at 11.0h. The first peak represented the hydration of silicate phases, while the second and third displayed that for aluminate phases, most likely conversion of ettringite to monosulphate and carbonation of the aluminate hydrate phases respectively. Up to 24 h, 12.2 J/g of cement of heat was released during the hydration of this cement.

Figure 3. Heat evolution of a neat ordinary Portland cement slurry over a period of 24 h, prepared at a w/c ratio of 0.36

In commuting the water demand and packing density of this cement slurry, the final packing density of this cement paste after centrifugal consolidation was 0.496, and the change in w/c ratio and density were 10.5 % and 3.0 % respectively (Table 4) at the compaction energy employed here.

3.1.2 Influence of the addition of superplasticizers

Rheological values give an indication of the flowability of the cement slurries. In the presence of superplasticizers, these values enable us to get a better understanding of the effectiveness of these dispersing agents, whether in their abilities to deglomerate and disperse the particles in solution or to reduce the water uptake for hydration, etc. When coupled with measurements such as packing density m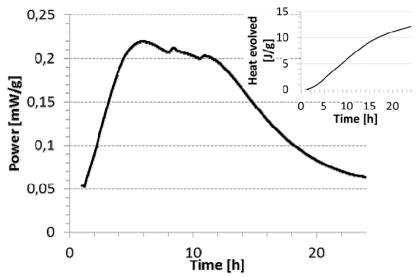easurements, these measurements enabled a better understanding of the working mechanism behind the performance of the superplasticizers.

Here, 0.2 %bwoc of each superplasticizer were added to the cement slurries to determine the effect of the dispersing agents on the rheological property of the cement pastes. For NAPh and LS, 0.4 %bwoc of these dispersing agents were also investigated to determine their dosage dependency. Whereas 0.1 %bwoc of the polycarboxylate based superplasticizers were selected as they are known to produce greater flowability. Table 3 and Figures 4 display the rheological findings of the ordinary Portland cement with the different types and dosages of superplasticizers. For all systems except for the addition of 0.2 %bwoc of NAPh, the initial μ_1 observed during run 1 decreased relative to that for a neat cement paste, whereas μ_2 remained approximately in the same magnitude. When the dosage of the polycarboxylate based superplasticizers was halved to 0.1 %bwoc, a slight increase in the viscosities of the cement pastes was observed, attributing to the decrease steric repulsion effect exerted by these polymers in solution. Likewise, when the dosage of NAPh was doubled, the viscosity of the cement slurry decreased, owing to the increase in electrostatic repulsion affected by the polymers adsorbed onto the surfaces of the cement particles. From here, two general observations can thus be made here. Firstly, the change in viscosity is not directly proportional to the dosages of superplasticizers added. Secondly, the impact on viscosity from the change in dosage was more significant when adding polycarboxylate based superplasticizers than when NAPh was added.

Figure 4. Flow resistance of cement pastes containing different dispersing agents in varying concentrations (0.1 to 0.4 % bwoc) prepared at a w/c ratio of 0.36

In the case of LS, a special observation was detected. Doubling the amount of LS added resulted in a doubling of μ_2, which is contrary to the performance for all the other superplasticizers. This observation signified that LS hastened the thickening of cement paste at a dosage of 0.4 %bwoc, and failed to plastify the cement paste. This abnormally had been observed in another work and can be attributed to the significant influence LS has on C_3A in the system. In presence of such high dosages of LS, the LS caused a rapid hydration of C_3A during the first 15 minutes of hydration, which result in rapid flash set [2]. In the case of other superplasticizers, the main influence of the plasticizers was on electrostatic surface adsorption with all the clinker phases to give rise to increase dispersion of the system. It is

known that the ordinary Portland cement (Norcem standard) possesses a relatively high amount of C_3A content ($\approx$ 7%bwoc according to Bogue).

Table 3. Rheological properties of the ordinary Portland cement slurries with added superplasticizers at a w/c ratio of 0.36 as a function of time

Superplasticizer		μ_1	μ_2	μ_1/μ_2	τ_d	τ_{s10s}	τ_{s10m}	$\Delta\tau_s$	FR_2	Hysteresis
Type	Amount [%bwoc]	[Pas]	[Pas]		[Pa]	[Pa]	[Pa]	[Pa]	[Nm/m³s]	[Nm/m³s]
RUN 1										
NAPh	0.2	6.20	0.30	21	240	155	-	-	37,600	1,850
LS	0.2	3.52	0.26	14	290	210	360	150	44,400	1,520
SRN	0.2	0.28	0.28	1	100	-	-	-	17,900	1,460
SX	0.2	0.08	0.23	0.3	30	161	85	-76	6,500	340
NRG	0.2	0.23	0.23	1	20	35	30	-5	6,000	510
NAPh	0.4	0.11	0.28	0.4	240	-	-	-	39,100	400
LS	0.4	2.02	0.47	4	200	185	340	155	33,700	2,960
SRN	0.1	1.86	0.33	6	160	172	298	126	27,100	2,200
SX	0.1	0.59	0.31	2	90	-	-	-	16,500	780
NRG	0.1	0.45	0.35	1	170	-	-	-	29,200	1,330
RUN 2										
NAPh	0.2	6.65	0.47	14	290	215	360	145	46,800	3,980
LS	0.2	1.11	1.11	1	110	110	235	125	29,300	6,960
SRN	0.2	0.55	0.36	2	90	-	-	-	17,400	1,490
SX	0.2	0.17	0.27	0.6	30	120	75	-45	6,900	490
NRG	0.2	0.25	0.25	1	30	45	45	0	6,900	70
NAPh	0.4	0.27	0.71	0.4	250	-	-	-	45,100	5,420
LS	0.4	1.24	1.24	1	120	150	265	115	30,900	4,220
SRN	0.1	1.86	0.35	5	170	180	300	120	28,500	460
SX	0.1	0.80	0.36	2	90	-	-	-	17,700	1,800
NRG	0.1	1.86	0.58	3	200	-	-	-	36,400	1,430
RUN 3										
NAPh	0.2	6.23	0.63	10	250	155	425	270	43,300	9,070
LS	0.2	0.81	0.81	1	50	45	125	80	16,400	2,090
SRN	0.2	0.49	0.37	1	90	190	175	15	17,900	1,500
SX	0.2	0.20	0.30	0.7	30	65	60	5	7,300	500
NRG	0.2	0.05	0.29	0.2	40	80	65	-15	9,500	-320
NAPh	0.4	2.26	0.74	3	280	410	735	325	50,700	3,300
LS	0.4	1.77	0.43	4	210	180	290	110	34,400	-5,420
SRN	0.1	1.79	0.38	5	170	190	290	100	30,300	350
SX	0.1	0.96	0.38	3	100	220	205	-15	19,300	1,700
NRG	0.1	2.80	0.88	3	200	400	540	140	39,600	1,460
RUN 4										
NAPh	0.2	7.22	0.50	14	250	135	530	395	41,200	6,510
LS	0.2	0.74	0.74	1	40	35	110	75	14,000	1,140
SRN	0.2	0.51	0.37	1	100	200	210	10	18,400	-260
SX	0.2	0.22	0.32	1	30	65	80	15	7,600	410
NRG	0.2	0.59	0.30	2	70	145	175	30	13,800	-710
NAPh	0.4	2.80	0.73	4	330	-	-	-	56,900	4,060
LS	0.4	1.79	0.45	4	220	190	305	115	35,600	-5,590
SRN	0.1	3.00	0.37	8	190	320	415	95	31,400	-40
SX	0.1	0.80	0.38	2	110	255	285	30	21,300	-240
NRG	0.1	2.36	1.00	2	150	120	465	345	32,700	860

The dynamic yield stresses of the cement slurries with added 0.2 %bwoc of superplasticizers were similar to the neat cement paste, except in the presence of SX-130 and NRG-700. In the

latter case, a drop in dynamic yield stress by an order of magnitude was observed, confirming that polymers with long side chain length can prevent agglomeration of the cement particles better via steric effect than through mere electrostatic repulsion. It was interesting to observe that for these two polymers, halving the dosage to 0.1 %bwoc greatly increased the dynamic yield stress of the cement slurries, unlike that for other superplasticizers including SRN (halving the dosages of SRN, SX and NRG resulted in a 1.6, 3 and 8.5 fold increase in dynamic yield stress respectively). This indicated that the plasticizing effectiveness of NRG and SX increased exponentially with dosages, indicating that the longer the side chain lengths of the polymer, the greater is the influence of dosage on its dispersing effectiveness. SRN which possessed much shorter side chain than the latter two polymers, on the other hand, disperse the cement clinkers less effectively.

Another observation here was the general consistency of the τ_d as a function of time. This indicated that the efficiency of the superplasticizers diminished with time, potentially due to consumption or coverage by the hydrating cement particles. Little can be drawn from the static yield stress as shear limit is reached in many cases. However, in general, the yield stress tends to be higher in presence of superplasticizers than for a neat cement paste. More interesting was the flow resistance of the cement slurries, which represented the overall work done in shearing the pastes. In general, the polycarboxylates decreased the overall FR_2 for the cement slurries significantly, dependent on the dosage added. Whereas NAPh and LS increased the work performed. Additionally, the inital FR_2 of cement slurry containing 0.2 %bwoc of LS was lower than that containing 0.4 %bwoc of LS, agreeing with the trend in viscosity of the cement paste containing this polymer as discussed earlier. This phenomenon was extended to their performance as a function of time, where more interestingly, the tendency to retain slump flow decreased in cement pastes containing 0.4 %bwoc of LS, while the slump improved in fluidity when only 0.2 %bwoc of LS was added. This could indicate that in presence of high dosages of LS (0.4 %bwoc), further reaction could occur after the initial surge to prolong the thickening effect arising from this polymer.

For further clarification of the rheological properties of the cement slurries, the packing density test on the cement slurries containing superplasticizers was performed. The rheological properties of cement slurries were greatly dependent on the availability of free water. Through this analysis, the amount of water retained by the cement paste, in presence or absence of superplasticizers can be investigated. Table 4 displays the change in the water demand and final packing density of the cement slurries, dependent on the type and dosage of superplasticizer added. The changes in the measured values before and after centrifugal consolidation are noted in Table 4 too. The measurement of packing density was performed within the first 15 minutes of the cement hydration, and thus only corresponded to the immediate rheological behaviour of the cement samples (run 1). In general, the addition of superplasticizers increased the amount of water retained by the cement paste while reducing the packing density of the cement matrix after centrifugal consolidation. Additionally, the packing density of the cement pastes varied when different type and amounts of superplasticizers were added.

Across the superplasticizers at a fixed dosing amount of 0.2 %bwoc of the dispersing agent, the water retaining capacity (and packing density) was the highest (lowest) for SX-130 > NRG-700 > SR-N > LS > NAPh respectively. From Figure 5 and 6 it can be observed that there is a correlation between the packing densities and flow resistances/ dynamic yield stress of the cement slurries when PCEs were added, but not in the case of NAPh or LS. The latter could be explained by a lack of sufficient data for analysis. In the former case, this correlation might arise due to a decrease in surface friction between particles in presence of an effective water layer bound to the hydrating cement particles. In presence of PCE superplasticizers, the water molecules can anchor both on the cement particle surfaces, but more effectively onto the hydrophilic PEO side chains of these superplasticizers which were already anchored onto the positively charged clinker surfaces of the cement grains via their

anionic backbone to reduce the friction between the neighbouring cement grains. In particular, the adsorption of superplasticizers onto the surfaces of C_3A further prevent topochemical hydration of C_3A, thus contributing to the increase in flowability of the cement slurry as less hydrate growth was to be expected during early hydration. On the other hand, no such correlation could be drawn from the viscosity versus packing density plot (Figure 7), signifying that the degree of water retention has a more direct impact on the flowability of the pastes than their stickiness.

Table 4. W/c ratios and densities of ordinary Portland cement slurries with and without the addition of superplasticizers after consolidation centrifugation

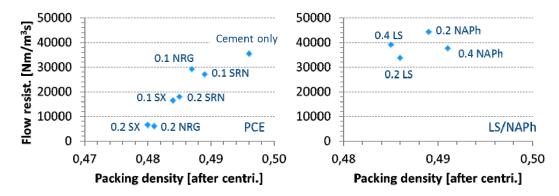| Superplasticizer Type	Amount [%bwoc]	w/c_{final}	$\Delta_{w/c}$ [%]	Packing density Before	after	$\Delta\%$	ρ_{after} [g/cm^3]	$\Delta\rho$ [%]
-	-	0.322	10.5	0.469	0.496	5.90	2.07	2.97
NAPh	0.2	0.330	8.4	0.469	0.491	4.68	2.05	2.35
LS	0.2	0.331	7.9	0.469	0.489	4.40	2.05	2.21
SRN	0.2	0.337	6.4	0.469	0.485	3.51	2.04	1.76
SX	0.2	0.345	4.3	0.469	0.480	2.33	2.03	1.17
NRG	0.2	0.343	4.8	0.469	0.481	2.64	2.03	1.32
NAPh	0.4	0.338	6.2	0.469	0.485	3.42	2.04	1.72
LS	0.4	0.336	6.7	0.469	0.486	3.70	2.04	1.86
SRN	0.1	0.332	7.9	0.469	0.489	4.35	2.05	2.19
SX	0.1	0.338	6.2	0.469	0.484	3.39	2.04	1.70
NRG	0.1	0.335	7.0	0.469	0.487	3.86	2.05	1.94

Figure 5. Correlation between packing density and flow resistance of cement slurries with added superplasticizers at different dosages, w/c = 0.36
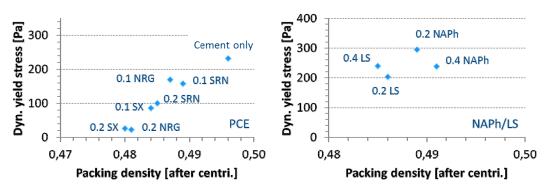

Figure 6. Correlation between packing density and dynamic yield stress of cement slurries with added superplasticizers at different dosages, w/c = 0.36

Further changes (increase or decrease) in the polymer dosages showed similar trend among the superplasticizers as observed when 0.2 %bwoc of superplasticizers was added, thus confirming the plasticizing mechanism at play. It should be noted that addition of superplasticizers can potentially alter the hydration rate and aspect ratio of the growth of hydrates topochemically. Therefore, further investigation could be performed to account for the final rheological property of the cement slurries.
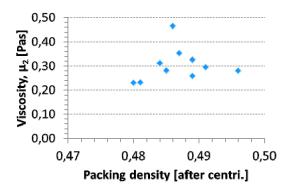

Figure 7. Correlation between packing density and viscosity of cement slurries with added superplasticizers at different dosages, w/c = 0.36

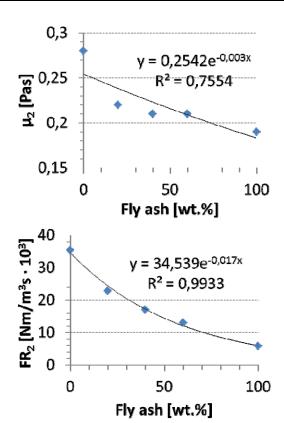## 3.2 Fly ash in blended cements

3.2.1 Effect of superplasticizers on cements possessing varying contents of fly ash

The addition of fly ash in cement is common practice in industry. To facilitate this, a detailed analysis of the effect of superplasticizers on the rheological properties of the ordinary Portland cement with increasing contents of fly ash (20, 40 and 60 wt.%) will be discussed here. For better understanding of the behaviour of blended cements, the pure fly ash slurry was investigated. Table 5 displays the rheological behaviour of a pure fly ash sample (100 wt.%) at w/FA ratio of 0.36. As compared to a neat cement slurry, the fly ash sample was more fluid and displayed a much lower flow resistance. The yield stress needed to shear the paste was also an order of magnitude lower, implying the low agglomeration tendency of fly ash particles in suspension. The relatively consistent rheology of the fly ash sample from run 1 to run 4 highlighted that little hydration or dissolution of the fly ash occurred under these working conditions here. Additionally, this can be attributed to the spherical nature of the fly ash particles as compared to the angularly shaped cement particles. When water demand and packing density was analysed, the fly ash slurry demonstrated a change of 14.0 % in w/c ratio and has a final packing density of 0.580 in contrast to the neat cement paste of 10.5 % and 0.496 respectively. This indicated that the affinity of fly ash for water is lower than cement clinkers, potentially due to the lack of hydration of the fly ash particles and their overall glassy nature. Additionally, the fly ash particles exhibited better packing density than the cement particles.

For cement samples possessing varying amounts of fly ash (20, 40 and 60 wt.%), the rheological properties were intermediate between that of the neat ordinary Portland cement paste and pure fly ash sample. In general, the higher the fly ash content, the lower the flow resistance of the cement slurries. It is important to also take into account the effect arising from the change in volume. In general, according to the Krieger-Dougherty equation, the rheological properties of the pastes are directly proportional to the volume occupied by the particles. When cement was replaced with fly ash by weight, a decrease in the volume of solid would be expected, thus resulting in a decrease in flow resistance of the pastes with increasing fly ash content. However, due to the great difference in rheological properties of fly ash and cement (e.g. yield stress), it can be concluded that the volume factor is not the main governing factor for the rheological properties of the pastes here.

Table 5. Rheological properties of the cement slurries with 20, 40, 60 and 100 wt.% of fly ash at a w/c ratio of 0.36 as a function of time without plasticizer

FA [wt.%]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m^{3}s]	Hysteresis [Nm/m^{3}s]
RUN 1									
20	2.58	0.22	12	150	60	220	160	22,800	510
40	1.51	0.21	7	110	45	130	85	17,100	-90
60	0.99	0.21	5	80	30	70	40	13,100	-520
100	0.84	0.19	4	26	6	11	5	5,840	-223
RUN 2									
20	2.90	0.24	12	180	60	220	160	26,600	1,710
40	1.83	0.26	7	120	45	130	85	19,800	1,000
60	1.23	0.25	5	90	30	50	20	15,500	500
100	0.94	0.22	4	30	6	11	5	6,680	31
RUN 3									
20	3.10	0.26	12	190	60	215	155	28,500	1,950
40	1.96	0.28	7	130	50	130	80	21,400	1,240
60	1.32	0.28	7	95	35	55	20	16,600	820
100	1.01	0.24	4	32	0	0.2	0	7,227	125
RUN 4									
20	3.28	0.30	11	200	60	255	195	29,800	2,170
40	2.09	0.28	7	140	50	130	80	22,400	1,190
60	1.44	0.29	5	100	30	95	65	17,500	920
100	1.05	0.26	4	34	0	0	0	7,590	201

Figure 8. Correlation between μ_2, τ_d and FR_2 values of the cement slurries to the amount of fly ash content present, w/c = 0.36 (from top left hand, clockwise)

Recalling the discussion in section 3.1, μ_2, τ_d and FR_2 can be effective parameters in describing the rheological parameters of the system. When these 3 parameters were plotted against the fly ash contents in the cement, a very good correlation was obtained for the latter

two using exponential fitting (Figure 8). Fitting of other values including static yield stress also gave relatively good fit, with a R^2 value of greater than 0.94. However, due to the frequency of reaching the limits of the measurements when analysing static yield stress and to ensure consistency with the neat cement slurry, the focus will be placed on the two parameters (τ_d and FR_2) when discussing the rheological effect of the fly ash system.

Table 6 to 8 presents the rheological data of cement slurries possessing 20, 40 and 60 wt.% fly ash in the presence of varying dosages of superplasticizers. In general, cement slurries containing higher amount of fly ash showed higher fluidity due to the dilution effect from fly ash in the cement. The addition of 0.2 %bwob of superplasticizers decreased the FR_2 for all cement slurries, but variations were detected in the viscosity and yield stress values. The influence of polycarboxylates on the rheological properties of the cement slurries outweighed that from NAPh and LS, similar to the situation in the neat ordinary Portland cement pastes. In all, the dispersing effectiveness of the superplasticizers on the cement containing fly ash, independent of the amount of fly ash present was as follow: NRG > SX > SRN > NAPh > LS. For slump retention, the trend was as follow: SRN > SX > NRG > NAPh ≈ LS. NRG proved to be a very good plasticizer, where no rheological data could be measured in a cement containing 60 wt.% fly ash when 0.2 %bwob of this polymer was added.

In the pure clinker cement, the FR_2 increased when NAPh and LS were added (Table 3). The slight decrease in FR_2 of the cement slurries from neat cement pastes to when NAPh and LS were added indicated that these dispersing agents interacted and dispersed the fly ash particles in solution. To justify this theory, a simple series of test was performed to determine the affinity of superplasticizers to pure fly ash through packing density analysis. 10 g of fly ash was added to water in a 50 mL falcon tube over half a minute at a w/c ratio of 0.36 in the presence of 0.4 %bwob of NAPh, LS and NAPh respectively. The mixture was manually shook for 1 min, let rest for 5 min and shook again for another 1 min. It was subsequently subjected to centrifugation at 4,000 rpm for 5 min and the packing density was calculated. A reference sample without superplasticizer was performed here too, due to the difference in shear speeds between manual mixing and high speed shearing. In the neat fly ash slurry, a packing density of 0.547 was attained, whereas 0.566, 0.546 and 0.613 were attained when NAPh, LS and NRG were added. This confirmed that introduction of superplasticizers to the fly ash slurry generate increase availability of free water in the system, which thus improved the fluidity of the fly ash slurry in the following order: LS < NAPh < NRG. In fact, much segregation was obtained in samples containing NRG and LS, and unclear supernatant were present in both NRG and LS, where NRG > LS. The results confirmed that the dispersing agents can adsorb onto the fly ash particles and induce a dispersing effect, both electrostatic (NAPh and LS) and steric (NRG), whereby the latter is stronger. In addition, the main mode of dispersion was through the availability of free water versus surface bound water.

In a blended cement system, the inhomogeneity of the surfaces of fly ash particles generated positive sites for electrostatic interaction between the incoming anionic polymer and fly ash particles. This in turn decreased the negative impact of the polymers on cement clinkers and coupled with the increase in overall repulsion of particles in solution to give a net drop in flow resistance of the cement slurries. This effect is particularly significant for LS addition, as interaction with fly ash particles decreases the negative influence it possesses on the C_3A clinker phases. It should, however be noted that as the interaction between superplasticizers and fly ash was not as strong as that with clinker phases, the degree of association of NAPh and LS and thus overall rheological behavior was thus more associated with the influence from cement clinker phases, particularly at lower fly ash contents (see Table 8 for the extent of influence).

Table 6. Rheological properties of the cement slurries with 20 wt.% fly ash in the presence of superplasticizers at a w/c ratio of 0.36 as a function of time

SP	Amount [%bwob]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
RUN 1										
NAPh	0.2	3.16	0.35	9	120	70	220	150	21,500	1,970
LS	0.2	1.68	0.33	5	120	70	235	165	21,200	1,500
SRN	0.2	0.47	0.26	2	40	130	115	-15	9,600	510
SX	0.2	0.17	0.17	1	10	25	30	5	3,500	190
NRG	0.2	0.15	0.15	1	5	0	10	10	2,300	270
NAPh	0.4	0.14	0.27	0.5	100	135	185	50	18,200	170
LS	0.4	2.52	0.26	10	150	160	275	115	25,200	970
SRN	0.1	0.69	0.32	2	80	95	170	75	16,100	920
SX	0.1	0.25	0.25	1	50	140	115	-25	10,100	430
NRG	0.1	0.14	0.27	0.5	60	85	105	20	11,600	600
RUN 2										
NAPh	0.2	4.04	0.42	10	140	60	220	160	25,000	3,740
LS	0.2	2.30	0.42	6	140	65	235	170	24,500	3,780
SRN	0.2	0.21	0.28	0.8	40	95	95	1	9,500	80
SX	0.2	0.21	0.20	1	10	20	30	10	3,700	400
NRG	0.2	0.17	0.17	1	5	5	10	5	2,600	150
NAPh	0.4	0.35	0.35	1	130	155	220	55	22,500	1,940
LS	0.4	2.65	0.25	11	160	160	310	150	26,200	1,870
SRN	0.1	0.92	0.33	3	90	85	150	65	16,700	310
SX	0.1	0.20	0.27	0.8	50	110	95	-15	10,500	40
NRG	0.1	0.26	0.28	0.9	70	90	130	40	13,700	230
RUN 3										
NAPh	0.2	4.48	0.41	11	160	70	255	185	26,800	3,680
LS	0.2	2.49	0.46	5	150	65	225	155	26,300	4,010
SRN	0.2	0.16	0.28	0.6	40	65	80	15	9,500	60
SX	0.2	0.22	0.21	1	10	10	30	20	3,800	300
NRG	0.2	0.18	0.18	1	10	0	0.2	0.2	3,300	-10
NAPh	0.4	1.16	0.42	3	140	150	260	10	25,200	2,690
LS	0.4	3.31	0.38	9	180	190	285	105	30,700	1,640
SRN	0.1	1.06	0.34	3	90	80	145	65	17,400	-20
SX	0.1	0.19	0.29	0.7	50	90	95	5	10,900	70
NRG	0.1	0.56	0.32	2	90	100	145	45	16,200	390
RUN 4										
NAPh	0.2	4.67	0.41	11	170	70	260	190	28,700	3,850
LS	0.2	3.79	0.45	8	150	65	225	160	25,700	3,800
SRN	0.2	0.12	0.28	0.4	40	65	80	15	9,500	-90
SX	0.2	0.23	0.22	1	10	10	15	5	3,900	320
NRG	0.2	0.20	0.20	1	20	10	15	5	4,500	-210
NAPh	0.4	1.33	0.44	3	150	175	315	140	27,400	2,970
LS	0.4	1.52	0.42	4	170	180	255	75	29,100	1,040
SRN	0.1	0.94	0.35	3	100	90	145	55	17,900	-50
SX	0.1	0.19	0.30	0.7	50	90	95	5	11,400	10
NRG	0.1	1.02	0.35	3	100	90	175	85	18,500	800

Table 7. Rheological properties of the cement slurries with 40 wt.% fly ash in the presence or absence of superplasticizers at a w/c ratio of 0.36 as a function of time

SP	Amount [%bwob]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
RUN 1										
NAPh	0.2	1.52	0.27	6	50	15	70	50	9,500	970
LS	0.2	0.74	0.30	2	50	20	225	205	10,400	640
SRN	0.2	0.17	0.18	1	9	10	20	10	3,400	150
SX	0.2	0.12	0.12	1	1	0	10	10	1,500	100
NRG	0.2	0.07	0.12	0.6	2	0	0	0	1,100	80
NAPh	0.4	0.19	0.19	1	40	55	95	40	7,800	-250
LS	0.4	0.32	0.32	1	80	95	160	65	15,000	550
SRN	0.1	0.21	0.25	0.8	30	35	65	30	7,000	240
SX	0.1	0.10	0.16	0.7	10	20	30	10	3,700	130
NRG	0.1	0.20	0.23	0.9	20	20	20	-1	5,900	290
RUN 2										
NAPh	0.2	2.06	0.38	5	60	20	80	60	12,500	1,760
LS	0.2	0.94	0.38	2	60	115	65	-50	12,400	2,000
SRN	0.2	0.20	0.20	1	9	10	10	0	3,500	140
SX	0.2	0.13	0.13	1	1	0	10	10	1,600	150
NRG	0.2	0.09	0.13	0.7	2	0	0	0	1,200	-140
NAPh	0.4	0.24	0.24	1	50	60	95	35	9,800	150
LS	0.4	0.37	0.37	1	90	105	150	45	16,800	1,520
SRN	0.1	0.19	0.27	0.7	30	35	55	20	7,300	70
SX	0.1	0.13	0.18	0.8	10	20	20	-1	4,100	130
NRG	0.1	0.21	0.25	0.9	30	30	35	5	7,200	-100
RUN 3										
NAPh	0.2	2.31	0.41	6	70	25	95	70	14,100	2,220
LS	0.2	1.10	0.42	3	60	20	65	45	13,500	1,460
SRN	0.2	0.21	0.21	1	8	0	15	15	3,600	140
SX	0.2	0.14	0.14	1	1	0	0.2	0.2	1,700	170
NRG	0.2	0.11	0.14	0.8	2	0	.2	0.2	1,400	-90
NAPh	0.4	0.28	0.28	1	50	55	95	40	11,200	460
LS	0.4	0.38	0.38	1	90	100	145	45	17,000	1,190
SRN	0.1	0.18	0.28	0.6	30	35	50	15	7,600	0
SX	0.1	0.15	0.19	0.8	10	10	15	5	4,300	100
NRG	0.1	0.23	0.28	0.8	40	35	50	15	9,000	-60
RUN 4										
NAPh	0.2	2.54	0.44	6	80	25	90	65	15,400	2,360
LS	0.2	1.23	0.44	3	70	20	65	45	14,200	1,340
SRN	0.2	0.22	0.22	1	10	0	15	15	3,700	110
SX	0.2	0.15	0.15	1	1	0	0	0	1,800	170
NRG	0.2	0.15	0.16	0.9	1	0	0	0	1,800	0
NAPh	0.4	0.31	0.31	1	60	55	95	40	12,100	830
LS	0.4	0.38	0.38	1	90	100	145	45	16,900	850
SRN	0.1	0.16	0.28	0.6	30	35	50	15	7,700	-60
SX	0.1	0.16	0.19	0.8	20	10	15	5	4,400	80
NRG	0.1	0.33	0.32	1	50	45	65	20	10,700	120

Table 8. Rheological properties of the cement slurries with 60 wt.% fly ash in the presence or absence of superplasticizers at a w/c ratio of 0.36 as a function of time

SP	Amount [%bwob]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
RUN 1										
NAPh	0.2	0.67	0.18	4	20	7	20	13	4,800	160
LS	0.2	0.61	0.21	3	20	6	10	4	5,200	160
SRN	0.2	0.09	0.10	0.9	0	0	0	0	1,100	30
SX	0.2	0.06	0.06	0.9	1	0	0	0	700	60
NRG	0.2									
NAPh	0.4	0.16	0.16	1	9	6	10	4	3,100	-20
LS	0.4	0.28	0.28	1	20	15	55	40	6,600	380
SRN	0.1	0.20	0.17	1	5	0	0	0	2,600	100
SX	0.1	0.13	0.13	1	3	6	10	4	1,900	60
NRG	0.1	0.17	0.17	1	2	0	0	0	2,200	130
RUN 2										
NAPh	0.2	0.87	0.22	4	25	8	20	12	6,000	380
LS	0.2	0.79	0.25	3	20	6	10	4	5,900	290
SRN	0.2	0.10	0.11	0.9	0	0	0	0	1,200	50
SX	0.2	0.04	0.07	0.7	1	0	0	0	600	110
NRG	0.2									
NAPh	0.4	0.18	0.18	1	10	10	20	10	3,900	-80
LS	0.4	0.28	0.28	1	30	30	55	20	7,300	230
SRN	0.1	0.21	0.19	1	5	0	0	0	2,800	140
SX	0.1	0.15	0.15	1	3	0	0	0	2,100	100
NRG	0.1	0.21	0.19	1	5	0	0	0	2,900	-70
RUN 3										
NAPh	0.2	1.00	0.24	4	30	9	15	6	6,600	520
LS	0.2	0.86	0.27	3	25	0	0.2	0.2	6,400	290
SRN	0.2	0.11	0.12	0.9	0	0	0.2	0.2	1,300	60
SX	0.2	0.05	0.06	0.8	1	0	0.2	0.2	700	20
NRG	0.2									
NAPh	0.4	0.20	0.20	1	15	10	30	20	4,600	-110
LS	0.4	0.30	0.30	1	30	20	65	35	7,700	250
SRN	0.1	0.22	0.19	1	5	0	0.2	0.2	2,900	110
SX	0.1	0.15	0.16	1	3	0	0.2	0.2	2,300	120
NRG	0.1	0.26	0.22	1	10	0	0.2	0.2	4,000	-180
RUN 4										
NAPh	0.2	1.10	0.26	4	30	8	20	12	7,100	560
LS	0.2	1.07	0.28	4	25	0	0	0	6,700	310
SRN	0.2	0.11	0.12	0.9	0	0	0	0	1,300	90
SX	0.2	0.05	0.07	0.7	1	0	0	0	700	80
NRG	0.2									
NAPh	0.4	0.22	0.22	1	20	10	30	20	5,300	-130
LS	0.4	0.31	0.31	1	30	20	65	45	8,000	210
SRN	0.1	0.22	0.20	1	5	0	0	0	3,000	90
SX	0.1	0.16	0.16	1	4	0	0	0	2,400	120
NRG	0.1	0.34	0.26	1	20	10	15	5	5,400	-260

An interesting observation was the dosage dependency of LS on its dispersing effectiveness. As observed before (section 3.1), cement slurries containing 0.4 %bwob of LS thickened as a function of time, but the contrary was observed when 0.2 %bwob of LS was added (Figure 9). For fly ash loaded cements, an increase in FR_2 by 19 % for a 20 wt.% fly ash loaded cement was observed right from the onset of hydration (Figure 9). In presence of 20 wt.% fly ash, the amount of clinker phases for interaction with LS decreased, thus a faster effect could be observed. A maximum was attained when 40 wt.% fly ash was replacing cement, and the change in flow resistance decreased when the cement contained 60 wt.% fly ash. This decrease could be explained by the excessive surfaces of fly ash present in the system that can interact positively with the LS, thus reducing impact on clinker phases and aided in dispersing the cementitious system. NAPh, on the other hand showed clear superplasticizing effect, whereby an increase in NAPh dosage resulted in increase in the fluidity of the cement slurry.
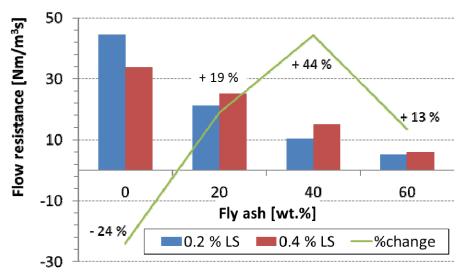

Figure 9. Flow resistance (FR_2) of cement slurries containing 0, 20, 40 and 60 wt.% fly ash with 0.2 or 0.4 %bwob of LS at a w/c of 0.36. Green line indicates the percentage difference in FR_2 between the cement slurries with 0.2 or 0.4 %bwob of LS.

The impact of the polycarboxylates on the FR_2 was inversely correlated to the amount of clinker phase present in the cement containing fly ash. Figure 10 presents the FR_2 of a cement containing the polycarboxylate based superplasticizer relative to the initial FR_2 of a cement paste without superplasticizer. In general, a decrease in the clinker content (more fly ash in the cement) and an increase in polymer dosage resulted in an increase in fluidity of the cement slurries, not proportional to the amount of cement clinker present. In the pure Portland cement, a reduction of FR_2 from 35,400 Nm/m^3s to 17,900, 6,500 and 6,000 Nm/m^3s were observed with the addition of 0.2 %bwob of SRN, SX and NRG respectively. When the cement containing 20 wt.% fly ash was utilized, the decrease in FR_2 were 22,800 Nm/m^3s to 9,600, 3,500 and 2,300 Nm/m^3s respectively, giving an approximate 80 % reduction (corresponding to the clinker content of the cement) in the improvement of flow resistance of the system. The reduction in flow resistance is greater when 0.2 %bwob of NRG was utilized, indicating that polycarboxylates possessing long side chains disperse fly ash better than the other two SX and SRN polymers, which possess shorter side chains. Additionally, the impact of increasing polymer dosage is more significant when NRG was utilized, followed by SX and SRN. These findings are similar to that in a pure clinker cement, indicating that the dispersing effect of the polymers on fly ash either mimic that of cement particles, or the influence of polycarboxylate-fly ash interaction is not significant in determining the rheology of the system.
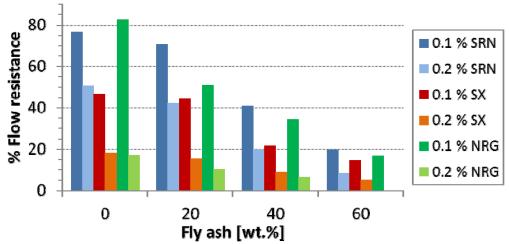
Figure 10. Flow resistance of cement slurries containing 0, 20, 40 and 60 wt.% fly ash in presence of polycarboxylate based superplasticzers relative to identical neat cement slurries at a w/c ratio of 0.36

When comparing the viscosity and yield stress of the cement slurries (20 wt.% FA and pure OPC), it can be observed that the findings are in line with the trend presented by FR_2. The main discrepancy lies in the apparent viscosity, μ_1 of NAPh and LS. This difference can be attributed to the time of measurements, where the viscosity is a reflection of the initial state in which the paste is, whereas flow resistance reflects the overall fluidity of the paste over the whole period of measurement.

Table 9 to 11 display the water demand and packing density of the cement containing 20, 40 and 60 wt.% fly ash after centrifugal consolidation. Generally, the packing density of the cement with added fly ash behaved like the ordinary Portland cement at lower fly ash content (20 wt.%), whereas it tends towards the characteristics of a pure fly ash slurry at higher fly ash content (60 wt.%). At low fly ash content, the rheological properties of the cement slurries can be correlated to the packing density by a generalization whereby an increase in packing density will result in a decrease in overall flow resistance of the cement pastes. At higher fly ash contents, the opposite was true as the role of fly ash gains importance. This change in tendency was particularly significant for polycarboxylate based superplasticizers (e.g. at a fly ash content of 20 wt.%, the change in packing density of cement in presence of 0.2 % bwoc of NAPh and NRG were 4.58 % and 3.91 % respectively, whereas in 60 % fly ash content, the change were 5.56 % and 12.14 % respectively, giving rise to potential bleeding in the system such as adding 0.2 %bwob of NRG to a cement containing 60 wt.% fly ash (Table 8). A surprising finding here was the high packing density of the cement containing 60 wt.% fly ash and 0.2 %bwob SX (0.632). During centrifugation, high amount of suspension was present in the supernatant, thus giving a 'false' high packing density. However, it was interesting to observe that a threshold balance (amount of fly ash and superplasticizer content) must be present to ensure a homogeneous and non-bleeding system.

3.2.2 Comparison between blended cement and cement with added fly ash

Till now, it can be observed that the rheological properties of cement with added fly ash in presence of superplasticizers was dependent on both the fly ash amount and also type of superplasticizer present. Often, it is insufficient to simply adjust the amount of superplasticizers added to the cement clinker content as interaction has been shown to occur between fly ash and superplasticizer. In such cases, particular attention was needed when polycarboxylate based superplasticizers were utilized due to their sensitivity.

Table 9. W/c ratios and densities of cement slurries possessing 20 % fly ash after consolidation centrifugation

Superplasticizer		w/c_{final}	$\Delta_{w/c}$	Packing density			ρ_{after}	$\Delta\rho$
Type	Amount [%bwob]		[%]	before	After	$\Delta\%$	[g/cm^3]	[%]
-	-	0.321	10.7	0.485	0.514	5.84	2.00	2.84
NAPh	0.2	0.329	8.5	0.485	0.508	4.58	1.99	2.22
LS	0.2	0.330	8.2	0.485	0.507	4.42	1.99	2.15
SRN	0.2	0.338	6.1	0.485	0.501	3.25	1.98	1.58
SX	0.2	0.343	4.7	0.485	0.497	2.47	1.97	1.20
NRG	0.2	0.334	7.3	0.485	0.504	3.91	1.98	1.90
NAPh	0.4	0.338	6.1	0.485	0.501	3.26	1.98	1.58
LS	0.4	0.337	6.4	0.485	0.502	3.42	1.98	1.66
SRN	0.1	0.332	7.7	0.485	0.505	4.11	1.98	2.00
SX	0.1	0.338	6.1	0.485	0.501	3.22	1.97	1.56
NRG	0.1	0.335	6.9	0.485	0.503	3.68	1.98	1.79

Table 10. W/c ratios and densities of cement slurries possessing 40 % fly ash after consolidation centrifugation

Superplasticizer		w/c_{final}	$\Delta_{w/c}$	Packing density			ρ_{after}	$\Delta\rho$
Type	Amount [%bwob]		[%]	before	after	$\Delta\%$	[g/cm^3]	[%]
-	-	0.319	11.5	0.501	0.531	6.07	1.94	2.85
NAPh	0.2	0.328	8.9	0.501	0.524	4.65	1.93	2.18
LS	0.2	0.327	9.3	0.501	0.525	4.84	1.93	2.28
SRN	0.2	0.334	7.1	0.501	0.519	3.67	1.92	1.72
SX	0.2	0.315	12.4	0.501	0.534	6.60	1.94	3.10
NRG	0.2	0.309	14.1	0.501	0.539	7.59	1.95	3.56
NAPh	0.4	0.332	7.6	0.501	0.521	3.97	1.92	1.86
LS	0.4	0.336	6.6	0.501	0.518	3.41	1.92	1.60
SRN	0.1	0.330	8.3	0.501	0.523	4.31	1.92	2.02
SX	0.1	0.333	7.6	0.501	0.521	3.96	1.92	1.86
NRG	0.1	0.332	7.6	0.501	0.521	3.97	1.92	1.86

Table 11. W/c ratios and densities of cement slurries possessing 60 % fly ash after consolidation centrifugation

Superplasticizer		w/c_{final}	$\Delta_{w/c}$	Packing density			ρ_{after}	$\Delta\rho$
Type	Amount [%bwob]		[%]	before	after	$\Delta\%$	[g/cm^3]	[%]
-	-	0.317	12.1	0.516	0.548	6.21	1.88	2.82
NAPh	0.2	0.321	10.9	0.516	0.544	5.56	1.88	2.52
LS	0.2	0.320	11.0	0.516	0.545	5.65	1.88	2.56
SRN	0.2	0.300	16.7	0.516	0.561	8.80	1.90	3.99
SX	0.2	0.223	38.0	0.516	0.632	22.55	2.02	10.22
NRG	0.2	0.280	22.4	0.516	0.578	12.14	1.93	5.50
NAPh	0.4	0.324	10.1	0.516	0.542	5.15	1.87	2.33
LS	0.4	0.327	9.1	0.516	0.539	4.61	1.87	2.09
SRN	0.1	0.325	9.8	0.516	0.542	5.00	1.87	2.27
SX	0.1	0.324	9.9	0.516	0.542	5.04	1.87	2.29
NRG	0.1	0.325	9.7	0.516	0.541	4.95	1.87	2.25

In this section, another factor which can influence the effectiveness of the superplasticizers, and thus the rheological properties of the resulting cement pastes is highlighted. This factor involved the point of blending together the fly ash and cement clinker. Industrially, the fly ash materials are premixed with the cement clinker prior to grinding, which is different from

the preparation method for the cements used earlier (fixed mass of fly ash was manually mixed with the ordinary Portland cement in the desired proportion). This section thus deals with this difference. As a fly ash cement, a cement containing ~18.2 wt.% fly ash was analyzed. The findings were then compared to that of an ordinary Portland cement (Table 3) and the cement containing 20 wt.% fly ash (Table 6).

Table 12 displays the rheological properties of the fly ash cement slurries in presence or absence of superplasticizers. The FR_2 of the neat fly ash cement slurry was 36,200 Nm/m^3s, ~ 60 % higher than the FR_2 of a neat cement paste containing 20 wt.% fly ash (22,800 Nm/m^3s) but similar to that of an ordinary Portland cement (35,400 Nm/m^3s). Comparing the efficiency of the dispersing agents at the dosage of 0.2 %bwob, the plasticizing effectiveness of the superplasticizers was as follow: SX > NRG > SRN > NAPH > LS. Whereas the slump flow retention is SRN > SX > NRG > LS ≈ NAPh. In general, the plasticizing effectiveness of these polymers was more similar to that of the ordinary Portland cement than the cement containing 20 wt.% fly ash.

This stark difference in rheological properties of a neat fly ash cement and a neat cement containing 20 wt.% fly ash (despite the similarity in fly ash content, 18.2 versus 20 wt.%) can be attributed to the nature of the packing behavior of the different materials. In the cement-fly ash mix, the cement clinker phases and fly ash particles were separated as individual particles. Therefore, the availability of fly ash to interact with water/ superplasticizers in solution will be dependent on the actual surface area on the fly ash particles in relation to the clinker phases. In our investigation, the surface area of fly ash and the ordinary Portland cement possessed similar surface areas. At onset of hydration, superplasticizers interacted rapidly with the positively charged clinker phases, which may be embedded in the cement particles. This in turn generated an overall advantage for the fly ash particles, which are fully exposed and ready for interaction. In such a situation, dilution of cement by addition of fly ash will be proportional to the amount of fly ash added (Table 5). In the flyash blended cement (faC), the surface is generally higher as it is finer ground and some of the coarser hollow fly as particles are crushed as well giving an even higher surface measureable with BET (outer and inner surface) but perhaps not reflected by the Blaine method (only "outer" surface).

The effectiveness of superplasticizers in greater details showed that the performance of 0.2 %bwob of NAPh and LS in the fly ash cement was worse than both that in the ordinary Portland cement and cement containing 20 wt.% fly ash. This is a puzzling trend and no real explanation could be given at this point of time. However, when the dosage was doubled, the performance of such dispersing agent normalized to give rheological data average of that between that of an ordinary Portland cement and the cement containing 20 wt.% fly ash. The slump loss retention effectiveness of NAPh/LS, regardless of dosage was similar to that in the case of polycarboxylates and can be attributed to the competitive adsorption of NAPh and LS for both the surfaces of fly ash and clinker phases. This signified that addition of fly ash has a direct impact on the time dependence performance of the superplasticizers, greater than the direct plasticizing effectiveness.

In the case of polycarboxylate superplasticizers, the performance of these polymers in the fly ash cement lies intermediate between that in an ordinary Portland cement and the cement containing 20 wt.% fly ash. This, coupled with the findings from NAPh and LS, potentially indicated that the affinity of polycarboxylate based superplasticizers for fly ash was higher than that of NAPh/LS, or alternatively, the degree of adsorbed NAPh/LS for the clinker phase outweighed for fly ash. In such a situation, the mechanism driving the process must be electrostatic in nature, where potentially, the fly ash surfaces could be more cationic charged in specific points, thus can act as an ideal anchor site for both incoming polycarboxylates and NAPh/LS, regardless of their anionicity. On the other hand, on the less positively charged surfaces of the clinker phases, the more anionic charge NAPh/LS can adsorbed better than the polycarboxylates. The adsorption of these polymers can also be governed by secondary adsorption mediated by Ca^{2+} present in the pore solution, similar to that occurring for other SCMs such as microsilica, etc. These two explanations could justify the higher

impact of increasing fly ash content on the effectiveness of the different superplasticizers (Table 6 to 8).

Table 12. Rheological properties of the fly ash cement slurries in the presence or absence of superplasticizers at a w/c ratio of 0.36 as a function of time

SP	Amount [%bwob]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
		RUN 1								
-	-	4.92	0.11	46	240	180	305	125	36,200	4,420
NAPh	0.2	3.18	0.40	8	300	215	305	90	46,100	1,150
LS	0.2	2.20	0.61	4	320	-	-	-	51,100	1,470
SRN	0.2	0.11	0.36	0.3	40	-	-	-	10,100	790
SX	0.2	0.14	0.17	0.8	9	20	45	25	3,400	320
NRG	0.2	0.22	0.22	1	10	15	30	15	4,000	520
NAPh	0.4	1.24	0.25	5	170	-	-	-	28,400	-70
LS	0.4	2.18	0.36	6	280	-	-	-	44,800	3,490
SRN	0.1	1.10	0.43	3	130	-	-	-	23,500	1,040
SX	0.1	0.37	0.33	1	70	-	-	-	13,600	1,230
NRG	0.1	0.73	0.43	2	120	245	285	40	22,700	1,770
		RUN 2								
-	-	2.80	0.18	15	140	135	305	170	25,100	4,070
NAPh	0.2	3.45	0.54	6	340	215	305	90	53,900	4,150
LS	0.2	2.19	0.92	2	320	-	490	-	55,100	2,080
SRN	0.2	0.14	0.38	0.4	40	110	85	-25	9,800	1,440
SX	0.2	0.16	0.19	0.8	8	15	30	15	3,400	380
NRG	0.2	0.25	0.25	1	10	20	30	10	4,900	110
NAPh	0.4	2.25	0.43	5	230	-	-	-	38,500	3,170
LS	0.4	3.46	0.82	4	230	-	-	-	43,200	6,120
SRN	0.1	1.29	0.48	3	140	-	-	-	25,500	720
SX	0.1	0.36	0.37	1	70	-	-	-	15,000	1,880
NRG	0.1	1.25	0.46	3	170	-	-	-	29,700	1,440
		RUN 3								
-	-	2.80	0.53	5	130	95	360	265	24,400	9,120
NAPh	0.2	4.22	0.44	10	320	215	360	145	50,300	9,790
LS	0.2	3.13	0.90	3	330	490	560	70	56,500	9,050
SRN	0.2	0.16	0.37	0.4	40	65	60	-5	9,500	110
SX	0.2	0.17	0.20	0.8	7	10	30	20	3,400	320
NRG	0.2	0.27	0.27	1	30	45	50	5	7,400	-440
NAPh	0.4	3.77	0.66	6	250	-	-	-	44,500	5,760
LS	0.4	3.12	0.79	4	230	300	400	100	42,400	2,540
SRN	0.1	1.10	0.51	2	140	200	255	55	26,800	620
SX	0.1	0.34	0.38	0.9	80	165	175	10	16,100	1,440
NRG	0.1	2.47	0.57	4.3	250	255	510	255	42,500	2,170
		RUN 4								
-	-	2.54	0.33	8	140	95	445	350	23,400	3,090
NAPh	0.2	5.75	0.63	9	300	215	530	315	49,600	12,830
LS	0.2	2.75	0.58	5	160	120	305	185	29,600	21,000
SRN	0.2	0.18	0.38	0.5	40	55	65	10	9,600	-30
SX	0.2	0.17	0.21	0.8	8	10	30	20	3,500	210
NRG	0.2	0.18	0.33	0.6	50	100	110	10	11,800	-1,120
NAPh	0.4	5.27	0.75	7	290	-	-	-	51,500	4,970
LS	0.4	3.11	0.73	4	230	280	400	120	41,700	2,070
SRN	0.1	1.16	0.50	2	150	210	335	125	28,300	-670
SX	0.1	0.48	0.36	1	80	165	175	10	16,500	40
NRG	0.1	3.47	0.68	5	290	280	-	-	49,500	4,550

Due to the high viscosity and general rheological properties of fly ash cement with added NAPh/LS, an additional experiment utilizing a dosage of 0.8 %bwob of NAPh was conducted (Table 13). It can be observed that ideal fluidity of the fly ash cement could be achieved with increased NAPh dosage, without any segregation of the cement pastes. A potential explanation could be the presence of sufficient polymers to cover both the clinker phases and also accommodate the fly ash, thus rendering an overall decrease in flow resistance of the system.

Table 13. Rheological properties of the fly ash cement slurry with 0.8 %bwob of NAPh as a function of time, w/c = 0.36

	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m^{3}s]	Hysteresis [Nm/m^{3}s]
RUN 1	0.16	0.16	1	13	34	53	20	3,700	50
RUN 2	0.18	0.18	1	15	45	53	9	4,300	70
RUN 3	0.20	0.20	1	19	45	64	19	5,100	40
RUN 4	0.21	0.21	1	24	56	64	8	5,900	-30

For better understanding of the rheological state of the fly ash cement, packing density was calculated and presented in Table 14. The change in packing density of this fly ash cement was lower than that of the other two systems as a result of increase in their fineness. In presence of superplasticizers, the same trend remained with the exception of the fly ash cement with 0.2 %bwob of NRG added. This signified that when cement particles and fly ash were in close proximity, an addition mechanism involving the ability of the cement particles in retaining water molecules was occurring. However, this effect observed could potentially be an outcome of prehydration or the presence of grinding agents. Clarification can be done by performing further thermal gravimetric analysis on the cement samples.

Table 14. W/c ratios and densities of fly ash cement slurries after consolidation centrifugation

Superplasticizer Type	Amount [%bwob]	w/c$_{final}$	$\Delta_{w/c}$ [%]	Packing density			ρ_{after} [g/cm^3]	$\Delta\rho$ [%]
				before	After	Δ%		
-	-	0.327	9.3	0.484	0.508	5.04	2.00	2.46
NAPh	0.2	0.331	7.9	0.484	0.505	4.28	1.99	2.08
LS	0.2	0.333	7.5	0.484	0.503	4.05	1.99	1.97
SRN	0.2	0.342	5.1	0.484	0.497	2.71	1.98	1.32
SX	0.2	0.346	3.8	0.484	0.493	1.98	1.97	0.96
NRG	0.2	0.340	5.5	0.484	0.498	2.92	1.98	1.42
NAPh	0.4	0.339	5.9	0.484	0.499	3.15	1.98	1.53
LS	0.4	0.337	6.4	0.484	0.500	3.44	1.98	1.68
SRN	0.1	0.336	6.6	0.484	0.501	3.50	1.98	1.71
SX	0.1	0.339	5.9	0.484	0.499	3.17	1.98	1.54
NRG	0.1	0.336	6.5	0.484	0.501	3.49	1.98	1.70
NAPh	0.8	0.339	5.7	0.484	0.499	3.03	1.98	1.49

3.3   Effect of using calcined marl in blended cement

The effect of calcined marl in blended cement was investigated next. In total, three different amounts of calcined marl was utilized; 20, 40 and 60 wt.% of total binder materials. At a w/c ratio of 0.36, the sample containing 60 wt.% of calcined marl was no longer fluid and no rheological properties could be measured (compression of sample between plates in rheometer required > 50 kN). The low water cement ratio was utilized to ensure a proper comparison with the fly ash system could be done, and the low fluidity of cement pastes containing calcined marl was compensated by the usage of higher dosages of superplasticizers. In this way, the effect of superplasticizers could be highlighted clearly.

As a start, the water retaining capacity of the calcined marl was determined by a simple set of experiments. Similar to that performed for fly ash samples, 15 g of calcined marl was added to water over half a minute in a 50 mL falcon tube. Here, no superplasticizer was present. Instead, the water amount was varied to give six different w/c ratios of 3.0, 2.0, 1.0, 0.5, 0.75 and 0.36 respectively. The mixture was then manually shook, let rest for 5 minutes and finally shook again for 1 minute. The sample obtained was centrifuged at 4,000 rpm for 5 min and the amount of supernatant obtained was recorded to determine the packing density of the calcined marl sample as shown in Figure 11. At the working w/c ratio of 0.36, no supernatant was observed. When the amount of water added was increased till a w/cM ratio of 3.0, the packing density of the compact calcined marl paste decreased, indicating an increase in water retaining capacity of the system. This signified that the water retaining capacity of the clay did not achieve its full capacity. In our systems, the minimum amount of calcined marl utilized was 20 wt.%. Assuming that the presence of cement clinkers had no influence on the water uptake capacity of the clay, the w/cM ratio which was present in this system (most diluted) would thus be 1.8. However, saturation point was yet to be attained. Therefore, under the working w/c ratio of 0.36, calcined marl can compete efficiently for water with the hydrating cement and the consumption or the availability of free water for fluidity of the cement slurries was thus a balance between the amount of clinkers that can undergo early hydration and the amount of calcined marl present.

Figure 11. Corelation between packing density and w/c ratio of a pure calcined marl system

Table 15 presents the rheological properties of cement containing 20 and 40 wt.% calcined marl respectively. A substitution of cement with 20 wt.% calcined marl displayed an initial FR_2 of 56,300 Nm/m^3s, which was about 1.5 times higher than that for an ordinary Portland cement. This indicated that the cement containing 20 wt.% calcined marl has a higher water retaining capacity than the cement, thus accounting for the decrease in fluidity of the cement. When the measurement was prolonged to run 2 on, a decrease in flow resistance to 17,000 Nm/m^3s in run 2 and finally 8,500 Nm/m^3s by run 4 was observed. This potentially indicated a delayed release of water from the calcined marl in the cement for prolonged dispersion of the cementitious system as mixing continued. However, contrary to the interpretation, for cement possessing a content of 40 wt% of calcined marl, the initial FR_2 was a low 6,800 Nm/m^3s, giving doubts to the hypothesis above. To clarify this point, a simple test to determine the water retaining capacity of calcined marl in presence of cement clinker was conducted. Water was added to a cement containing 20 wt.% calcined marl at a w/c ratio of 0.36 as per procedure and subjected to centrifugation 10 min and 30 min after mixing. The amount of supernatant obtained at the two different time intervals was compared and found that similar amount of water (within a ± 5 % error limit) was centrifuged out after 30 min, thus ruling out the mechanism of an increase in availability of free water from reversible binding to the calcined marl as a possible reason. Additionally, due to relatively consistent amount of free water present in the system after 10 or 30 min, it can be concluded that the hydration or adsorption of water by the binders was a very rapid process.

Table 15. Rheological properties of the cement slurries with 0, 20 and 40 wt.% of calcined clay at a w/c ratio of 0.36 as a function of time (60 and 100 wt.% calcined clay samples showed no fluidity, thus no rheological measurements were possible)

cM [wt.%]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m^{3}s]	Hysteresis [Nm/m^{3}s]
RUN 1									
0	4.06	0.28	14	230	105	255	150	35,400	790
20	3.38	0.49	7	370	215	360	145	56,300	2,450
40	0.18	0,18	1	30	45	110	70	6,800	4,450
RUN 2									
0	4.35	0.32	13	280	110	255	145	42,000	3,950
20	2.31	0.63	4	65	50	155	105	17,000	13,640
40	0.20	0.06	3	40	35	110	75	6,500	760
RUN 3									
0	3.63	0.99	4	160	95	420	325	31,200	-15,540
20	1.44	0.37	4	45	30	95	65	10,800	3,060
40	0.43	0.08	5	40	35	95	55	6,800	230
RUN 4									
0	1.25	0.60	2	60	20	110	90	15,100	8,340
20	1.13	0.30	4	35	25	95	70	8,500	1,510
40	0.26	0.27	1	20	25	70	40	5,700	2,010

To further quantify these cement systems, the water demand and packing densities of cement slurries utilized for rheological measurements were explored and displayed in Table 16. Increase in clay content clearly increased the water retaining capacity of the system, while a decrease in packing density was observed. In relation to the rheological properties, cement containing 60 wt.% and the pure calcined marl sample showed no flow at all. This clearly indicated that the sharp increase in FR_2 of the cement paste was a result of rapid water retention by the calcined marl present in the cements. The decrease in FR_2 as observed for cements containing 20 wt.% calcined marl after the first run, and also at a higher calcined marl content of 40 wt.% further confirmed that the reliability of the rheometer instrument was no longer sound after a $FR_2 > 56,000$ Nm/m^{3}s, instead of the cutoff value of 42,000 Nm/m^{3}s as observed in Table 2. Also, when analysing the rheological properties of the clay, it is important to take into account both the water retaining capacity of the calcined marl or the calcined marl/cement system and also the threshold limit of the rheometer.

The influence of superplasticizers is presented in Table 17. 0.2 and 0.4 %bwob of superplasticizers were added to all systems. Here, a higher dosage of superplasticizers was utilized to ensure dispersion of the cement paste as a result of the high water retaining capacity of the calcined marl. In general, adding a dosage of 0.1 %bwob of superplasticizers proved to be too low to fluidize the cements containing calcined marl. Only SX was able to sufficiently disperse the cement for rheological measurements at the low dosage of 0.1%bwob (Table 17). A high FR_2 of 42,700 Nm/m^{3}s was registered for the cement system, which decreased rapidly due to thickening of the paste beyond the measurement range of the rheometer. This effective dispersion of cement paste by SX, however differed from that observed for a neat cement paste containing only clinker, or with fly ash. For the latter two systems, NRG was always performing better than the other polycarboxylates and also NAPh/LS due to an increase in steric repulsion with its longer side chains. Here, the better performance of SX polymer which possessed an intermediate side chain length and charge density signified that long side chain lengths may interfere with the workability of superplasticizers such as NRG in a calcined marl loaded cement system. In general, smectite clays are known to intercalate poly(ethylene oxide). Some characteristics of layered structures may persist in the calcined marl, rendering superplasticizers with long side chain length vulnerable for consumption and unavailable for exerting the dispersing effect. On the

other hand, polymers possessing shorter side chain lengths were less vulnerable to intercalation by the clay, thus allowing a higher proportion to be available for effective dispersion.

Table 16. W/c ratios and packing densities of cement slurries possessing 0, 20, 40, 60 and 100 wt.% calcined marl after consolidation centrifugation

cM	w/c$_{final}$	$\Delta_{w/c}$	Packing density			ρ_{after}	$\Delta\rho$
[wt.%]		[%]	Before	after	Δ%	[g/cm^3]	[%]
0	0.322	10.5	0.469	0.496	5.90	2.07	2.97
20	0.327	9.3	0.478	0.502	5.10	2.02	2.52
40	0.331	8.0	0.487	0.507	4.26	1.98	2.06
60	0.353	1.9	0.495	0.500	0.97	1.92	0.46
100	0.356	1.2	0.512	0.515	0.57	1.85	0.26

When 40 wt.% calcined marl cement sample was investigated, the flow resistance decreased drastically which can be attributed to the premature hardening of the cement paste in the rheometer. However, comparing to the neat cement paste containing 40 wt.% calcined marl, the hardening was also less (as observed in the drop in FR$_2$). This is in agreement with the results observed for 0.2 %bwob of SX added.

Table 17. Rheological properties of the cement slurry with 20 and 40 wt.% calcined marl in the presence of 0.1 %bwob SX-130 as a function of time, w/c = 0.36

RUN	cM [wt.%]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR$_2$ [Nm/m^{3}s]	Hysteresis [Nm/m^{3}s]
1	20	3.26	0.45	7	255	-	-	-	42,700	2,650
	40	0.36	0.40	0.9	80	-	-	-	15,900	6,600
2	20	0.42	0.84	0.5	65	120	300	180	19,600	11,760
	40	0.13	0.28	0.5	60	85	245	160	11,400	5,100
3	20	0.39	0.60	0.6	75	90	225	135	17,700	2,410
	40	0.02	0.24	0.1	50	65	175	110	10,700	1,800
4	20	0.45	0.56	0.8	80	90	225	135	17,800	1,200
	40	0.03	0.24	0.1	60	80	175	95	11,900	800

From Table 18, addition of superplasticizers improved the fluidity of the cement slurries and the plasticizing effectiveness of the superplasticizers at an added dosage of 0.4 wt.% could be derived from the FR$_2$ of the cement pastes as follow: SX > NRG > SRN > NAPh > LS, similar to an ordinary Portland cement or in the case of cement containing fly ash. The effectiveness of the dispersing agents on slump retention was SRN ≈ SX > NRG > LS > NAPh. When comparing the effect of dosage addition, increase in dosage of the polycarboxylates generated a decrease in FR$_2$, signifying better dispersion whereas for NAPh and LS, an increase in shear stress was needed to shear the paste. The trend for these findings was in line with that for the ordinary Portland cements. However, at a closer look, it can be observed that the performance of polycarboxylates at the lower dosage of 0.2 %bwob was much higher than that observed for the ordinary Portland cements, whereas the deviation was less for NAPh and LS.

As discussed earlier, calcined marl retained water in great quantity, thus resulting in the rapid decrease in fluidity of the cement pastes. This was clearly reflected in the performance of polycarboxylates addition, where addition of calcined marl to the cement system resulted in a proportional decrease in workability of the pastes. On the other hand, the FR$_2$ observed for cement pastes with added NAPh and LS signified that calcined marl may interact with these polymers which can effectively result in a decrease in water uptake by the calcined marl. Alternatively, the interaction of NAPh/Ls with calcined marl may influence other

hydration mechanism occurring such as delay in flash setting of C_3A or alteration of the hydrate morphologies in the presence of calcined marl and the polymers.

Table 18. Rheological properties of the cement slurries with 20 wt.% calcined marl in the presence or absence of superplasticizers at a w/c ratio of 0.36 as a function of time

SP	Amount [%bwob]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
RUN 1										
NAPh	0.2	1.51	0.33	5	190	215	360	145	32,400	10,050
LS	0.2	2.48	0.80	3	190	145	385	240	35,600	9,140
SRN	0.2	1.91	0.43	4	150	-	-	-	26,900	1,190
SX	0.2	0.93	0.38	2	90	-	-	-	17,800	290
NRG	0.2	0.23	0.35	0.7	150	-	-	-	25,700	-240
NAPh	0.4	1.84	0.25	7	280	-	-	-	43,500	240
LS	0.4	3.21	0.46	7	320	-	-	-	49,900	3020
SRN	0.4	0.36	0.33	1	50	90	320	230	11,400	180
SX	0.4	0.27	0.22	1	8	15	65	50	3,700	190
NRG	0.4	0.26	0.25	1	0	0	10	10	2,800	220
RUN 2										
NAPh	0.2	2.41	0.35	7	170	155	500	345	28,800	6,750
LS	0.2	2.91	0.53	5	140	130	275	145	26,400	6,640
SRN	0.2	0.49	0.42	1	160	-	-	-	28,500	730
SX	0.2	1.10	0.46	2	120	-	-	-	23,400	1,890
NRG	0.2	0.60	0.45	1.3	130	-	-	-	24,300	12,020
NAPh	0.4	0.64	0.64	1	70	100	285	185	17,500	16,140
LS	0.4	3.10	0.90	3	265	235	385	150	46,200	7,590
SRN	0.4	0.28	0.41	0.7	50	-	-	-	12,000	-10
SX	0.4	0.32	0.27	1	8	15	75	60	4,100	390
NRG	0.4	0.37	0.29	1	4	6	30	24	3,900	230
RUN 3										
NAPh	0.2	1.73	0.74	2	65	70	220	150	18,400	14,440
LS	0.2	2.04	0.38	5	125	120	240	120	22,700	2,860
SRN	0.2	0.73	0.61	1	160	335	510	175	30,700	-680
SX	0.2	1.58	0.64	2	155	-	-	-	31,000	3,360
NRG	0.2	0.44	0.51	0.9	95	120	225	105	19,600	2,090
NAPh	0.4	0.50	0.50	1	65	65	225	160	15,300	4,270
LS	0.4	0.72	0.72	1	100	120	225	105	22,800	2,860
SRN	0.4	0.34	0.43	0.8	50	-	-	-	12,700	2,070
SX	0.4	0.35	0.29	1	8	10	80	70	4,500	430
NRG	0.4	0.33	0.32	1	25	55	255	200	7,200	-500
RUN 4										
NAPh	0.2	0.40	0.40	1	50	45	130	85	11,600	4,220
LS	0.2	2.86	0.34	8	110	90	210	120	120,000	2,270
SRN	0.2	0.06	0.57	0.1	160	335	525	190	30,800	-650
SX	0.2	1.89	0.71	3	200	-	-	-	37,900	3,730
NRG	0.2	0.43	0.38	1	80	90	190	100	16,100	2,270
NAPh	0.4	0.45	0.45	1	65	65	210	145	15,000	2,490
LS	0.4	0.52	0.52	1	60	65	145	80	14,800	3,560
SRN	0.4	0.35	0.37	1	55	-	-	-	12,700	1,590
SX	0.4	0.37	0.31	1	9	10	80	70	4,800	430
NRG	0.4	0.15	0.31	0.5	85	-	-	-	16,600	-1,630

To test the theories, the availability of water as a result of rapid water adsorption by the calcined marl was investigated. As a first step in investigation, the packing densities of pure calcined clay with and without three different superplasticizers were compared at two

different w/c ratios, 0.36 and 0.75. 0.36 is the working w/c ratio in this investigation, whereas 0.75 is the first w/c ratio where fluidity of the calcined marl could be observed during manual mixing. Most investigations were conducted at w/c ratio of 0.75 due to the ease of detecting the effect of superplasticizers. Figure 12 displays an increase in packing density (~1 %) when 0.4 %bwob of NRG was added to the pure calcined marl, signifying that in a water deficient environment, addition of NRG increased the amount of free water. At the same dosage at a w/c ratio of 0.75, the reverse occurred. Similarly, addition of 0.4 %bwob of LS and NAPh resulted in a change in packing density. From this investigation, it can observed that addition of superplasticizers, regardless of the type affect the water retaining capacity of the clay. Therefore, addition of superplasticizers in cements containing calcined marl will induce an effect on the availability of water amount directly. Increased polymer dosage led to an increase in water demand at w/c ratio of 0.75, whereas different superplasticizers affect the degree of water uptake by the cement paste differently.

Figure 12. Packing density of pure calcined marl as a function of w/c ratio and dosages of superplasticizers added

Table 19 and 20 displayed the rheological properties of the cements containing 40 and 60 wt.% calcined marl respectively. For cements containing higher calcined marl percentage (60 wt.%), superplasticizers up to a dosage of 0.8 % bwob were utilized to enable fluidity of the samples. As observed, in cement containing more than 40 wt.% calcined marl, no effective rheological data could be obtained from the addition of 0.2 %bwob of NAPh or LS. However, the lack in dispersing ability can be compensated by increasing the polymer dosage proportionally to achieve a sustainable dispersion without segregation (0.4 %bwob at 40 wt.% calcined marl content whereas 0.8 %bwob at 60 wt.% calcined marl). For the polycarboxylates, the rheoligcal properties could be accounted for as a combination effect of the water retaining capacity of the calcined marl and also the dispersing effectiveness of the superplasticizers on the clinker phases. Little interaction or dispersion from these superplasticizers on the calcined marl was to be expected. An anomaly is the performance of SX, where 0.2 %bwob of SX appeared to disperse better than when 0.4 %bwob of the same PCE was added. No suitable explanation could be given at this point of investigation.

Table 19. Rheological properties of the cement slurries with 40 wt.% calcined marl in the presence or absence of superplasticizers at a w/c ratio of 0.36 as a function of time

SP	Amount [%bwob]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
RUN 1										
NAPh	0.2	0.54	0,10	5	20	45	110	70	4,700	3,240
LS	0.2	0.19	0,19	1	20	20	65	40	5,700	2,890
SRN	0.2	1.33	0,78	2	430	-	-	-	71,500	6,080
SX	0.2	1.09	0,65	2	260	-	-	-	46,000	2,730
NRG	0.2	0.75	0,43	2	170	-	-	-	30,300	12,610
NAPh	0.4	0.13	0,67	0.2	70	180	-	-	18,200	12,060
LS	0.4	0.38	0.38	1	70	90	180	90	14,100	3,640
SRN	0.4	0.17	0.42	0.4	40	-	-	-	10,400	390
SX	0.4	0.17	0.31	0.5	30	-	-	-	7,300	270
NRG	0.4	0.39	0.38	1	20	-	-	-	7,800	-210
RUN 2										
NAPh	0.2	0.12	0.12	1	20	30	80	50	4,700	1,230
LS	0.2									
SRN	0.2	0.63	1.30	0.5	160	-	-	-	39,400	23,240
SX	0.2	0.44	0.80	0.6	110	-	-	-	26,200	19,340
NRG	0.2	0.43	0.43	1	50	85	190	105	12,100	9,720
NAPh	0.4	0.19	0.29	0.7	50	90	300	210	11,100	6,080
LS	0.4	0.28	0.28	1	60	85	150	65	12,000	570
SRN	0.4	0.14	0.49	0.3	50	-	-	-	12,400	1,990
SX	0.4	0.39	0.41	1	40	-	-	-	11,300	1,970
NRG	0.4	2.80	0.78	4	170	-	-	-	35,200	2,030
RUN 3										
NAPh	0.2	0.06	0.06	1	30	30	80	50	4,800	600
LS	0.2									
SRN	0.2	0.13	0.93	0.1	120	220	655	430	29,000	7,070
SX	0.2	0.25	0.47	0.5	90	145	415	270	18,700	6,260
NRG	0.2	0.27	0.27	1	40	55	110	55	8,700	2,900
NAPh	0.4	0.17	0.25	0.7	60	90	270	180	12,400	2,180
LS	0.4	0.28	0.28	1	60	65	145	75	11,600	990
SRN	0.4	0.70	0.55	1	70	-	-	-	16,100	2,860
SX	0.4	0.94	0.61	2	90	-	-	-	20,200	5,670
NRG	0.4	2.66	1.14	2	220	-	-	-	46,600	16,190
RUN 4										
NAPh	0.2	0.12	0.12	1	30	35	75	40	5,700	270
LS	0.2									
SRN	0.2	0.06	0.60	0.1	90	120	335	215	19,500	5,830
SX	0.2	0.34	0.56	0.6	90	135	350	220	19,100	2,990
NRG	0.2	0.23	0.23	1	40	35	95	60	8,100	860
NAPh	0.4	0.20	0.24	0.8	80	100	285	185	14,100	1,690
LS	0.4	0.28	0.28	1	60	65	145	75	11,600	700
SRN	0.4	0.27	0.64	0.4	90	-	-	-	21,200	3,950
SX	0.4	0.15	0.68	0.2	140	-	-	-	29,700	9,600
NRG	0.4	2.46	1.10	2	290	-	-	-	55,400	11,600

Table 20. Rheological properties of the cement slurries with 60 wt.% calcined marl in the presence or absence of superplasticizers at a w/c ratio of 0.36 as a function of time

SP	Amount [%bwob]	μ_1 [Pas]	μ_2 [Pas]	μ_1/μ_2	τ_d [Pa]	τ_{s10s} [Pa]	τ_{s10m} [Pa]	$\Delta\tau_s$ [Pa]	FR_2 [Nm/m³s]	Hysteresis [Nm/m³s]
		RUN 1								
NAPh	0.8	2.99	1.99	2	210	-	-	-	54,100	5,760
LS	0.8	1.46	0.63	2	150	180	350	175	26,400	9,070
SRN	0.4	2.51	0.47	5	200	-	-	-	35,300	-1,290
SX	0.4	0.72	0.52	1	150	-	-	-	28,500	80
NRG	0.4	2.62	0.43	6	300	-	-	-	50,100	-3,510
SX	0.2	1.92	0.14	14	130	-	-	-	21,300	2,180
		RUN 2								
NAPh	0.8	1.46	0.52	3	200	-	-	-	35,500	23,490
LS	0.8	1.58	0.68	2	150	160	405	245	27,300	-3,660
SRN	0.4	0.10	0.81	0.1	80	-	-	-	21,600	23,100
SX	0.4	0.90	1.29	0.7	150	-	-	-	37,100	32,110
NRG	0.4									
SX	0.2	0.75	0.32	2	50	195	-	-	10,600	11,210
		RUN 3								
NAPh	0.8	0.82	0.82	1	150	300	-	-	30,700	15,630
LS	0.8	1.17	0.48	2	130	165	385	215	23,700	-2,730
SRN	0.4	0.15	0.47	0.3	70	165	590	425	15,700	7,270
SX	0.4	0.65	0.19	3	220	-	-	-	32,700	14,860
NRG	0.4									
SX	0.2	0.83	0.07	12	80	155	415	260	12,700	2,880
		RUN 4								
NAPh	0.8	1.62	0.30	5	250	245	685	440	36,700	1,460
LS	0.8	1.25	0.47	3	140	155	335	180	24,300	-2,480
SRN	0.4	0.56	0.41	1	80	145	415	270	15,900	2,880
SX	0.4	0.73	0.94	0.8	200	-	-	-	39,500	10,970
NRG	0.4									
SX	0.2	0.36	0.26	1	60	120	305	180	12,500	3,790

Table 21 to 23 display the water demand and packing densities of the cement containing 20, 40 and 60 wt.% calcined marl after centrifugal consolidation. Generally, the packing density of the cement with added calcined marl behaved similar to the ordinary Portland cement at lower calcined marl content (20 wt.%), whereas it tends towards the characteristics of a pure calcined marl slurry at higher calcined marl content (60 wt.%). At low calcined marl content and in the presence of 0.2 %bwob of superplasticizer, the rheological properties of the cement slurries can be correlated to the packing density by a generalization whereby increase in packing density will result in a decrease in overall flow resistance of the cement pastes. However, this trend deviated when the dosage of superplasticizers was doubled. In general, increase in the dosage of superplasticizers resulted in a decrease in the percentage change of packing density for all system. This indicated that availability of free water was greater when more superplasticizers were added, thus an increase in fluidity (thus lower flow resistance, Table 17 to 20) was observed. Among the superplasticizers utilized, doubling the dosage of NRG displayed the greatest reduction in packing density (3.25 % to 0.93 %), indicating that the polyethylene side chains may interact with clay particles to increase the amount of water uptake. This, when coupled with the observation from Table 18 proved that the decrease in FR_2 of the cement pastes containing polycarboxylates was a result of the availability of free water in the system.

Table 21. W/c ratios and densities of cement slurries possessing 20 % calcined marl after consolidation centrifugation

| Superplasticizer | | | | Packing density | | | | |
Type	Amount [%bwob]	w/c_{final}	$\Delta_{w/c}$ [%]	Before	after	Δ%	ρ_{after} [g/cm^3]	$\Delta\rho$ [%]
NAPh	0.2	0.330	8.2	0.478	0.499	4.49	2.02	2.21
LS	0.2	0.332	7.8	0.478	0.498	4.22	2.01	2.08
SRN	0.2	0.338	6.1	0.478	0.493	3.28	2.00	1.62
SX	0.2	0.341	5.4	0.478	0.492	2.90	2.00	1.43
NRG	0.2	0.338	6.0	0.478	0.493	3.25	2.00	1.60
NAPh	0.4	0.334	7.1	0.478	0.496	3.86	2.01	1.90
LS	0.4	0.335	6.8	0.478	0.496	3.70	2.01	1.82
SRN	0.4	0.344	4.4	0.478	0.489	2.33	2.00	1.15
SX	0.4	0.342	5.0	0.478	0.491	2.70	2.00	1.33
NRG	0.4	0.354	1.8	0.478	0.482	0.93	1.98	0.46
SX	0.1	0.334	7.2	0.478	0.497	3.93	2.01	1.94

Table 22. W/c ratios and densities of cement slurries possessing 40 % calcined marl after consolidation centrifugation

| Superplasticizer | | | | Packing density | | | | |
Type	Amount [%bwob]	w/c_{final}	$\Delta_{w/c}$ [%]	Before	after	Δ%	ρ_{after} [g/cm^3]	$\Delta\rho$ [%]
NAPh	0.2	0.334	7.3	0.487	0.506	3.88	1.98	1.88
LS	0.2	0.335	6.9	0.487	0.505	3.70	1.97	1.79
SRN	0.2	0.337	6.3	0.487	0.503	3.35	1.97	1.62
SX	0.2	0.339	5.9	0.487	0.502	3.12	1.97	1.51
NRG	0.2	0.337	6.5	0.487	0.504	3.46	1.97	1.68
NAPh	0.4	0.336	6.8	0.487	0.504	3.59	1.97	1.74
LS	0.4	0.336	6.6	0.487	0.504	3.48	1.97	1.69
SRN	0.4	0.347	3.7	0.487	0.496	1.94	1.96	0.94
SX	0.4	0.345	4.2	0.487	0.497	2.19	1.96	1.06
NRG	0.4	0.347	3.7	0.487	0.496	1.93	1.96	0.93
SX	0.1	0.335	6.8	0.487	0.504	3.62	1.97	1.76

Table 23. W/c ratios and densities of cement slurries possessing 60 % calcined marl after consolidation centrifugation

| Superplasticizer | | | | Packing density | | | | |
Type	Amount [%bwob]	w/c_{final}	$\Delta_{w/c}$ [%]	Before	after	Δ%	ρ_{after} [g/cm^3]	$\Delta\rho$ [%]
NAPh	0.2	0.347	3.6	0.495	0.505	1.87	1.92	0.89
LS	0.2	0.340	5.6	0.495	0.510	2.90	1.93	1.38
SRN	0.2	0.342	5.1	0.495	0.509	2.66	1.93	1.26
SX	0.2	0.340	5.4	0.495	0.509	282	1.93	1.34
NRG	0.2	0.342	5.1	0.495	0.508	2.62	1.93	1.24
NAPh	0.4	0.344	4.5	0.495	0.507	2.31	1.93	1.10
LS	0.4	0.340	5.7	0.495	0.510	2.94	1.93	1.40
SRN	0.4	0.342	4.9	0.495	0.508	2.55	1.93	1.21
SX	0.4	0.344	4.4	0.495	0.507	2.29	1.93	1.09
NRG	0.4	0.342	5.1	0.495	0.508	2.64	1.93	1.25
NAPh	0.8	0.340	5.5	0.495	0.509	2.83	1.93	1.35
LS	0.8	0.342	5.0	0.495	0.508	2.57	1.93	1.22
SX	0.1	0.342	5.1	0.495	0.508	2.63	1.93	1.25
NRG	0.1	0.340	5.7	0.495	0.510	2.95	1.93	1.40

At higher calcined marl contents, the opposite is true as the role of calcined marl gained importance. For cements possessing 60 wt.% calcined marl, an increase in change in packing density was observed when the polymer dosage was doubled, similar to that observed for 100 wt.% calcined marl at a w/c ratio of 0.36 (Figure 11). This indicated that at such a high polymer dosage, characteristic interactions of polymers with calcined marl dominated. An intermediate change in packing density was observed when 40 wt.% calcined marl was added in the system. The findings here indicated that the affinity of superplasticizers for calcined marl and cement clinkers may be similar, thus inducing such an effect according to the ratio of clinker versus calcined marl present in the system.

3.4   Calorimetry analysis of the cement slurries

3.4.1 Heat analysis of ordinary Portland cement with added superplasticizers

The calorimetry analysis of the ordinary Portland cement in presence and absence of superplasticizers up to 24 h are displayed in Figure 13 to 15. In a neat cement paste, three main peaks of hydration were detected at 5.2h, 8.0h and 11.2h, with a rate of heat production of 0.22 mW/g, 0.21 mW/g and 0.20 mW/g respectively (Figure 3). The first peak of hydration corresponded to the general hydration of silicate phases, particularly alite while the second and third peak corresponded to the hydration of aluminate phases. The former correspond to the conversion of ettringite to monosulphate as gypsum were depleted, whereas the latter is a display of carbonation of the layered aluminate phases. The cumulative heat evolved by 24h of hydration of this cement sample was 12.1 J/g. Figure 13 compares the effect of the type of superplasticizers added (at a fixed dosage of 0.2 %bwob) on the hydration of cement pastes. Figure 14 compares the effect of polymer dosages (0.2 and 0.4 % bwoc) when NAPh and LS were added to the system, whereas Figure 15 highlights the effect of polymer dosages (0.1 and 0.2 % bwoc) when polycarboxylate based superplasticizers were added. The amount of polycarboxylate added was lower than NAPh/LS due to their higher efficiency in dispersing the cement.

From Figure 13, two main observations can be drawn. Firstly, all superplasticizers increased the induction period of the cement paste, which may indicate that the setting of the cement is retarded. The extent of retardation was greatest for SX > SRN > LS > NRG > NAPh, where a delay of between 0.2 to 4 h was observed. In general, superplasticizers can act as pseudo retarders when they adsorb onto the surfaces of cement grains by inhibiting subsequent topochemical hydration. The retardation effect of LS is well known and can be attributed to adsorption onto the surfaces of alite clinkers, resulting in a delay in hydration. In the case of the polycarboxylates superplasticizers, the presence of smaller polymers or oligomers such as free ethylene oxides oligomers or polymers as a by-product from synthesis could have affected this retardation. In such a case, the amount of smaller molecules in this class of polymers was as follow: SX > SRN > NRG. This hypothesis can be confirmed by performing GPC analysis. Also, recalling the observation from rheological investigations on superplasticizers addition to cement containing calcined marl, the addition of SX effectively outperformed all the other superplasticizers by displaying dispersing effectiveness at a polymer dosage of 0.1 %bwob (Table 17). The main influencing factor may potentially be attributed to the presence of such small molecules, which can intercalate between the existing interlayer spaces of the clay particles and thus hinder its water retaining capacity to enhance the fluidity of the cements observed through rheological measurements during early hydration.

The second observation from Fig. 9 is related to the maximum rate of change in hydration. When superplasticizers were introduced, the maximum rate of heat released increased somewhat and broadened for the first peak, but increased significantly more for the second peak. This signified that in the presence of superplasticizers, the rate of hydration of silicate phases increases and spreads over time, while the conversion of ettringite to monosulphate increases more abruptly. In such a situation, it could be explained that up to 1d cement hydration, the superplasticizers remained coated on the alite particles, thus prolonging the dormant period before hydration of the silicate phases. On the other hand, hydrated phases such as ettringite which were less affected by the superplasticizers (potentially due to the rapid uptake of these polymers by non-hydrate phases right at the start of hydration), can thus a higher rate of dissolution and conversion. Another potential explanation for the higher rate of conversion could be attributed to the availability of the sulphate ions in solution. A sudden surge in superplasticizers uptake by the surfaces of the clinker phases could potentially render SO_4^{2-} free for the more time consuming process of hydration reaction such as ettringite formation. Therefore, when more ettringite were formed in the

presence of superplasticizers during the initial hydration, the rate of conversion at the later age will be higher due to the need to re-establish equilibrium.

In general when the induction period ends and when plasticizers are included, the hydration rate increases relative to neat cement pastes simply due to the dispersion effect of the cement agglomerates leading to more "free surface" where hydrates can grow.

Figure 13, right displayed the overall heat released in cement hydration, whereby the addition of superplasticizers increased the cumulative heat production from the cement hydration. In presence of low retardation such as when NRG was added, the total heat released by the cement paste exceeded that for a neat cement paste as early as 7.5h, just 2 hours after the initial hydration peak of a neat cement paste was observed. This potentially indicates that a higher 1d strength of the cement paste with NRG was to be expected than that for a neat cement paste. All plasticizers lead to higher cumulative hydration heat relative to neat cement at 24 h, in spite of some prolongation of the induction period, simply due to the dispersion of cement agglomerates leading to more "free surface".
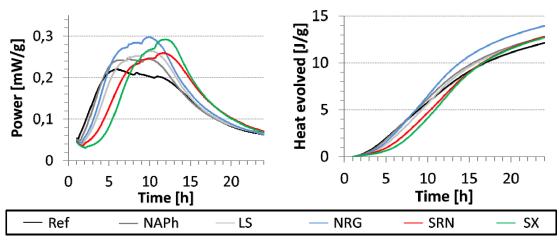

Figure 13. Heat evolution of ordinary Portland cement slurries hydrated in the presence and absence of 0.2 %bwoc of superplasticizers over a period of 24 h, prepared at a w/c ratio of 0.36
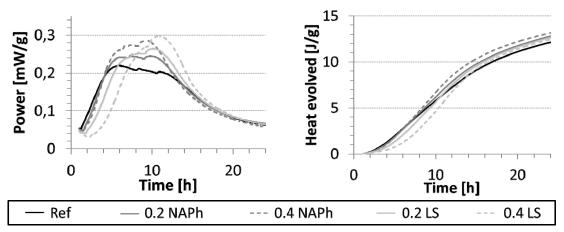

Figure 14. Heat evolution of ordinary Portland cement slurries hydrated in the presence and absence of 0.2 and 0.4 %bwoc of NAPh and LS over a period of 24 h, prepared at a w/c ratio of 0.36

When comparing the dosage effect of NAPh and LS, two phenomena could be observed (Figure 14). Firstly, doubling the dosage of these polymers resulted in a marked increase in the 2nd peak of the hydration profile. This can be attributed to an increase in conversion of

ettringite to monosulphate with increase NAPh/LS addition, potentially due to the competitive sorption of superplasticizers and SO_4^{2-} by the CAH phases. Secondly, the induction period was prolonged (i.e setting retarded) significantly (by 2.2h) when the dosage of LS was doubled, while the same amount of heat released at 24 h was maintained. On the other hand, in the case of NAPh dosing, no significant retardation, but a slightly increase in cumulative heat (from 12.5 J/g to 13.1 J/g) was detected. This implied that the interaction of LS and NAPh occur via different mechanisms with the cement. As known, LS can interact majorly with the C_3A and alite phases present in the cement. Therefore, the delay in hydration with increasing LS addition can be attributed to the inhibtion of surface hydration of the alite particles. In the case of NAPh, higher anionicity could potentially be a reason for this observation. Therefore, the interaction of NAPh is less phase specific than LS, resulting in a spread in points of interaction, thus preventing the retardation effect as shown for LS.

In the case of dosing polycarboxylate based superplasticizers at 0.1 and 0.2 %bwoc (see Fig. 11), little retardation was observed when NRG was added, whereas for SRN and SX, the retardation of cement hydration was proportional to the dosage of polymer added, higher the polymer content, the greater the retardation of the cement paste. In terms of heat released, not much changes was observed in SRN and SX, whereas an overall increase in NRG resulted in an increase in cumulative heat from 13.0 J/g to 14.0 J/g.
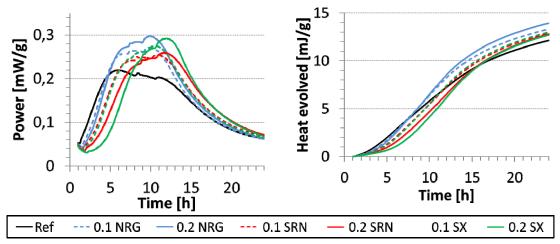

Figure 15. Heat evolution of ordinary Portland cement slurry hydrated in the presence and absence of 0.1 and 0.2 %bwoc of polycaboxylates based superplasticizers over a period of 24 h, prepared at a w/c ratio of 0.36

3.4.2 Heat profiling of cement containing fly ash

With the knowledge of the hydration of ordinary Portland cement in the presence or absence of superplasticizers, the effect of fly ash addition on cement hydration was next analyzed. Figure 16 presents the rate of heat evolution of cement possessing 20, 40, 60 and 100 wt.% fly ash and a fly ash cement relative to the neat ordinary Portland cement paste (denoted as 'Std' in the figure). Effectively, the ordinary Portland cement displayed a high heat of evolution (12.1 J/g) while the pure fly ash slurry produced little or negligible heat and only achieved a cumulative heat of hydration of 1.8 J/g up to 24h (Table 24). In the case of cements with varying fly ash dosages, it can be observed that the rate of heat evolution falls between that observed for ordinary Portland cement and fly ash and decreased proportionally to the amount of cement clinkers and fly ash present. The total heat evolved may then be presented in the given equation:

$$\text{Heat evolved (J/g)} = (1 - FA\%)H_{std} + (FA\%)H_{FA} \tag{1}$$

Where FA% is the fraction of fly ash present in the cement, H_{std} is the heat evolved from the hydration of the ordinary Portland cement, while H_{FA} is the heat evolved from the hydration

of the pure fly ash slurry. Table 24 displayed the measured and calculated heat evolved during hydration of the different binder systems, based on equation 1. In general, the decrease in heat evolved can be attributed to the dilution effect of the fly ash, which also explained the improvement in rheological performance of the cement pastes with increasing fly ash content (Table 5). However, at higher fly ash content, the extent of hydration calculated deviated from the measured value, thus signifying that hydration of fly ash played an important role here. At lower fly ash content, this SCM only acts mainly as a filler.

Table 24. Cumulative heat evolved corresponding to figure

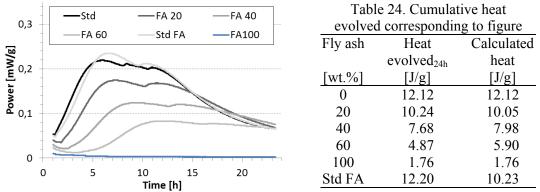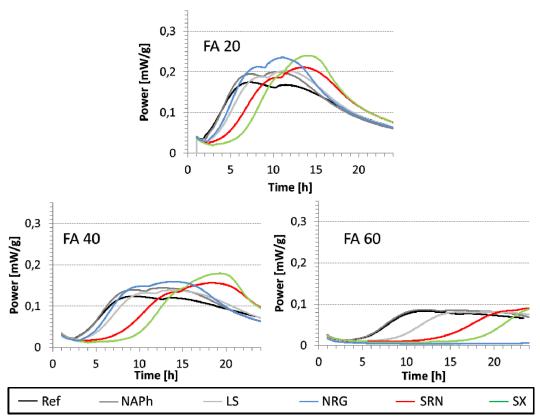| Fly ash	Heat evolved$_{24h}$	Calculated heat
[wt.%]	[J/g]	[J/g]
0	12.12	12.12
20	10.24	10.05
40	7.68	7.98
60	4.87	5.90
100	1.76	1.76
Std FA	12.20	10.23

Figure 16. Rate of heat evolution of cement containing 0, 20, 40, 60 and 100 wt.% fly ash and fly ash cement (18.2 wt.% fly ash) over a period of 24 h, prepared at a w/c ratio of 0.36

In the presence of 0.2 %bwob of superplasticizers (see Fig. 13), retardation of the cement hydration was observed in the following order: SX > SRN > LS > NRG > NAPh. This trend followed that for the ordinary Portland cement (Figure 13), and thus the hydration profile of such cements can be attributed to the hydration of the Portland cement. As discussed earlier, hydration of fly ash was negligible. When the fly ash contents were increased, the hydration of cement was further retarded, e.g. NRG addition resulted in a retardation of the first hydration peak of the cements from 5h, 6h, 14h and finally to non-detectable for samples possessing 0, 20, 40 and 60 wt.% fly ash. The great extent of retardation when 0.2 %bwob of NRG was added indicated that this polymer have reduced affinity for fly ash as compared to other polymers. Additionally, the delay in hydration can be accounted for by the decrease in clinker phases which could interact with superplasticizers. As a result, at constant superplasticizer addition, the amount of clinker phases such as silicate phase will undergo higher probability of surface interaction with the superplasticizers, rendering a further delay in the hydration process. It can be recalled that fly ash was determined to interact with the superplasticizers during early age hydration (Figure 8). However, from these findings, the superplasticizers can potentially desorb from the fly ash surfaces and undergo further interaction with clinker phases. Therefore, two conclusions can be made here. Firstly, though superplasticizers interacted with fly ash, this process is reversible. Secondly, clinker phases possess a higher affinity for the superplasticizers than the fly ash particles. The lack of retardation of cement pastes (regardless of fly ash content) in presence of NAPh signified that the minor retardation in an ordinary Portland cement was adjusted and diluted by the introduction of fly ash. Therefore, fly ash addition, at the expense of heat released (and thus strength of concrete) could assist to minimize the impact of retardation from NAPh addition.

Another observation from Figure 17 is the change in maximum rate of heat evolution. The addition of superplasticizers resulted in an increase in heat evolution, particularly of the second hydration peak. In general, this was only detected for cements containing 20 and 40 wt.% fly ash due to the high extent of retardation in presence of fly ash. For all samples, the total heat evolved was the greatest with NRG addition and least for SX (11.5 J/g and 10.4 J/g respectively).

Figure 17. Rate of heat evolution of cement with 20, 40 and 60 wt.% fly ash containing 0.2 %bwob of different superplasticizers over a period of 24 h, prepared at a w/c ratio of 0.36
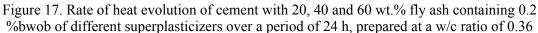
Figure 18 displays the rate of heat evolution when NAPh/LS were added to the cement slurries. The performance of LS on the cements was in lined with that of the ordinary Portland cement, thus confirming that interaction of LS with both fly ash and clinker phases were similar. In general, the amounts of heat evolved by 24h were lower when more LS as added to the cement (Table 25). However, this can be accounted for by the delay in hydration, rendering heat evolved by 24h to be only partial heat evolved during hydration of such cementitious systems. On the other hand, when NAPh was added, the effect was both dosage and fly ash concentration dependent. When a cement containing 20 wt.% fly ash was involved, little retardation was observed when 0.1 or 0.2 %bwob of NAPh was added. When the amount of fly ash in the cement was increased to 40 wt.%, a slight decrease in initial rate of hydration was observed. This effect enhanced to achieve a delay in hydration of ~4h when 60 wt.% fly ash was present, indicating that the presence of NAPh in excessive fly ash retards the hydration of silicate phases, potentially due to the higher affinity of NAPh for the silicate phases over that of fly ash. Therefore, in presence of increased fly ash and NAPh, less clinker was present to interact with the higher dosage of NAPh, thus greater surface areas of the silicate phases could be covered, resulting in a decrease in hydration. Here, the affinity of NAPh is thus higher for clinker phases, particularly silicates as compared to the fly ash.

The impact of halving the dosage of polycarboxylates added can be observed in Figure 19. In cement containing 20 and 40 wt.% of fly ash, the decrease in retardation effect were similar to that in an ordinary Portland cement. The main difference is the extent of change. In a fly ash loaded cement, it can be observed that increasing the polymer dosage from 0.1 to 0.2 %bwob, the delay in hydration increased, confirming that presence of fly ash affected the hydration profile of the cement. An interesting observation is the effect of NRG on a cement containing 60 wt.% fly ash. As discussed earlier, NRG reacted preferentially to the clinker phases than fly ash, both in the pure fly ash system and when 0.2 %bwob was added to a

cement holding 60 wt.% fly ash. When 0.1 %bwob of NRG was added to this cement, no retardation was observed, similar to the situation when no fly ash or only 20 and 40 wt.% fly ash were present in the cement. This marked an interesting phenomenon as it suggested that a threshold dosage of such polymer must be added before retardation of the cement hydration will be observed. Therefore, application wise, usage of a dosage of less than 0.2 %bwob is recommended to prevent excessive retardation and thus decrease in early strength of the concrete. Or alternatively, higher dosages of such polymer can be employed when greater retardation is needed.
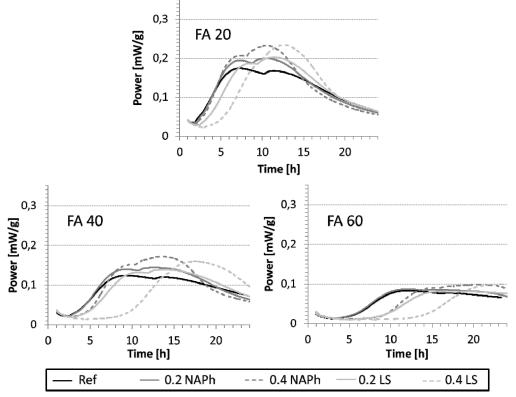

Figure 18. Rate of heat evolution of cement with 20, 40 and 60 wt.% fly ash hydrated in the presence of 0.2 and 0.4 %bwob of NAPh or LS over a period of 24 h, prepared at a w/c ratio of 0.36

As observed so far, the hydration profile of the different cements in presence of different superplasticizers follow a trend similar to that of the rheological properties. In general, an improvement in fluidity of the paste (lower FR_2 value) is coupled with a decrease in overall heat evolved or delay in the rate of cement hydration. This can be tied closely to the amount of fly ash present, and also the type of superplasticizer utilized, Greater influence from NAPh and NRG was observed in cements containing higher fly ash contents, while the impact from polymers such as LS remained consistent regardless of fly ash content and worked simply based on a dilution effect in the presence of fly ash.
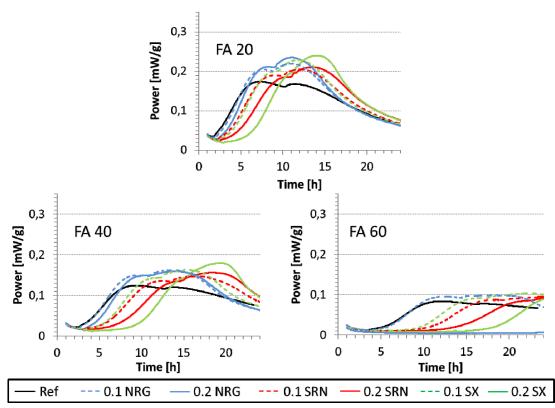
Figure 19. Rate of heat evolution of cement with 20, 40 and 60 wt.% fly ash hydrated in the presence of 0.1 and 0.2 %bwob of polycarboxylate based superplasticizers over a period of 24 h, prepared at a w/c ratio of 0.36
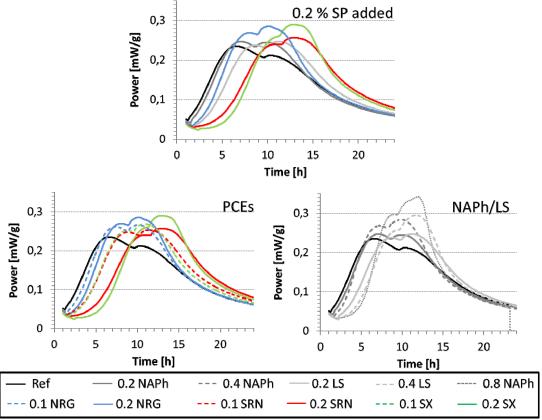
Table 25. Cumulative heat evolved of the cement slurries containing 20, 40 and 60 wt.% fly ash in presence of superplasticizers, prepared at a w/c ratio of 0.36

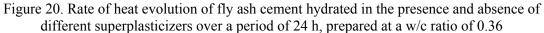| Fly ash	Superplasticizer		Heat evolved$_{24h}$	Fly ash	Superplasticizer		Heat evolved$_{24h}$
[wt.%]	Type	[%bwob]	[J/g]	[wt.%]	Type	[%bwob]	[J/g]
20	NAPh	0.2	10.87	20	NAPh	0.4	11.21
20	LS	0.2	10.58	20	LS	0.4	10.36
20	SRN	0.2	10.65	20	SRN	0.1	10.82
20	SX	0.2	10.40	20	SX	0.1	11.05
20	NRG	0.2	11.47	20	NRG	0.1	11.38
40	LS	0.2	7.89	40	LS	0.4	6.91
40	NAPh	0.2	8.45	40	NAPh	0.4	8.61
40	SRN	0.2	7.61	40	SRN	0.1	8.00
40	SX	0.2	7.27	40	SX	0.1	8.27
40	NRG	0.2	8.59	40	NRG	0.1	8.94
60	LS	0.2	4.11	60	NAPh	0.4	4.82
60	NAPh	0.2	5.26	60	LS	0.4	3.24
60	SRN	0.2	2.82	60	SRN	0.1	3.92
60	SX	0.2	1.76	60	SX	0.1	4.60
60	NRG	0.2	0.46	60	NRG	0.1	5.68

From rheological data, it was observed that the behaviour of a fly ash cement is similar to that of an ordinary Portland cement, reasons discussed in previous section. Here, the hydration profile of a neat fly ash cement showed an overall heat evolution of 12.20 J/g (Table 26), similar to the cumulative heat evolved for the ordinary Portland cement (12.1 J/g). Likewise, the impact of superplasticizers closely resemble that for an ordinary Portland cement, and deviates from the cement containing 20 wt.% fly ash. These results confirmed

that a direct link between the hydration profile and rheological properties of fly ash blended cements can be attained. Also, the impact of superplasticizers in cement on the overall hydration or rheological properties is not dependent on the amount of fly ash present, but the extent of fly ash with available surfaces for interaction with the water or superplasticizers in the cement slurry.

Table 26. Cumulative heat evolved of the fly ash cement slurries in presence of superplasticizers, prepared at a w/c ratio of 0.36

Superplasticizer		Heat evolved$_{24h}$	Superplasticizer		Heat evolved$_{24h}$
Type	[%bwob]	[J/g]	Type	[%bwob]	[J/g]
LS	0.2	12.12	NAPh	0.4	12.79
NAPh	0.2	12.34	LS	0.4	12.17
SRN	0.2	12.20	SRN	0.1	12.64
SX	0.2	12.04	SX	0.1	12.46
NRG	0.2	12.91	NRG	0.1	12.89
NAPh	0.8	12.31	-	-	12.20

Figure 20. Rate of heat evolution of fly ash cement hydrated in the presence and absence of different superplasticizers over a period of 24 h, prepared at a w/c ratio of 0.36

3.4.3 Heat profiling of cement containing calcined marl

Next, the hydration profiles of cement containing calcined marl were investigated. Similar to fly ash system, the cumulative heat evolved from these cements decreased with increased calcined marl. The hydration of calcined marl remained low and yield a minimum heat of 0.62 J/g after 24h. This indicated that calcined marl when alone, underwent little hydration. In fact, due to the small magnitude of the hydration, the increase in heat could be simply a factor of dissolution of ions from the surfaces of the calcined marl grains. Another observation is the constant initial change in rate of hydration. When the amount of calcined

marl in the cement increased to 40 wt.%, the rate of silicate hydration remained the same. Therefore, this signified that the only limiting factor here is the amount of Si phase present, whereas conditions for hydration remained the same. A decrease in the rate of hydration was observed only for cement containing 60 wt.% calcined marl. This could be explained by the dilution effect of the clinker phases in presence of excessive calcined marl. Final reaction of the silicate phase remained dependent on the presence of silicate phase in the cement.

Two other interesting observations could be observed here. Firstly, the extent of decrease in heat evolution here is less than that in cements containing fly ash. For example, a substitution of 20 wt.% fly ash or calcined marl resulted in a cumulative heat evolved of 10.24 and 10.87 J/g. This difference increased when 60 wt.% of the supplementary materials were present (4.87 and 5.75 J/g respectively). In the fly ash systems, it was deduced that increasing amount of fly ash in the system led to a dilution effect, thus the cumulative heat evolved can be deduced by a simple equation (1). In the calcined marl system, however, this direct correlation is not valid, especially since that the heat of hydration of calcined marl by 24h is only one third that of fly ash hydration (0.62 versus 1.76 J/g). This indicated that firstly, water consumption by calcined marl is a mechanical process, where no heat was generated (Table 16). And secondly, during the hydration of cement containing calcined marl, reaction between the cement clinkers and calcined marl occurred to generate excess heat, which was either absent or less dominating in that of cements containing fly ash. This is confirmed by the change in hydration profile of the second peak when 60 wt.% calcined marl is present in the cement. An idea of the reactive phases present in calcined marl can be obtained by running an XRD analysis on the sample. Such a change could potentially occur due to the change in aspect ratio of the ettringite formed, thus altering the heat evolved during their conversion to monosulphate. Additionally, a suitable equation to represent the heat evolved from the calcined marl is as follow:

$$\text{Heat evolved (J/g)} = (1 - cM\%)H_{std} + (cM\%)H_{cM} + \Phi_{rxn} \tag{2}$$

Where $cM\%$ is the fraction of fly ash present in the cement, H_{std} is the heat evolved from the hydration of the ordinary Portland cement, H_{cM} is the heat evolved from the hydration of the pure calcined marl paste, while Φ_{rxn} represent the extent of reaction between calcined marl and clinker phases. In this equation, the contribution from H_{std} dominates. In general, the decrease in heat evolved can be attributed to the decreased in the availability of clinker phases for hydration, while the discrepancy in the decrease can be attributed to the side reaction between clinker phases and calcined marl. This side reaction, coupled with the rapid uptake of water by calcined marl explained the decrease in rheological performance of the cement pastes with increasing calcined marl content (Table 17).

Table 27. Cumulative heat evolved corresponding to figure

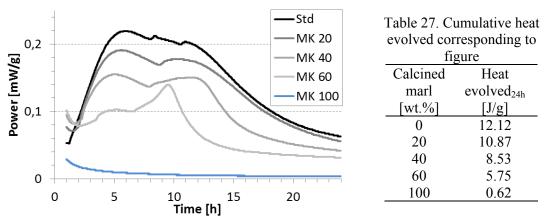| Calcined marl [wt.%]	Heat evolved$_{24h}$ [J/g]
0	12.12
20	10.87
40	8.53
60	5.75
100	0.62

Figure 21. Heat evolution of cement containing 0, 20, 40, 60 and 100 wt.% calcined marl over a period of 24 h, prepared at a w/c ratio of 0.36

The first set of investigations on the influence of superplasticizers on the hydration of cement containing calcined marl can be observed from Figure 22. Here, the influence of addition of 0.2 %bwob of superplasticizers is displayed. In general, an increase in calcined marl in the cement resulted in a shortening of the delay in the induction period of the cement relative to the ordinary Portland cement. In fact, only the addition of SX and NRG displayed signs of retardation of this period when 20 and 40 wt.% calcined marl were present respectively. This could be accounted for by the additional reaction between cement clinker and calcined marl, which prevent the inihibition of hydration by superplasticizers. In such a situation, this indicated that silicate phase is a major phase interacting with the calcined marl. Other clinker may undergo interaction too. However, no such conclusions could be drawn from the findings here. When comparing the effect of superplasticizer dosages, the hydration profile of cements with added NAPh and LS were similar to that of the ordinary Portland cement samples (Figure 22). This confirmed that in such a system, the superplasticizers do not influence the hydrating behavior of calcined clay, but only worked and affected the clinker phases.
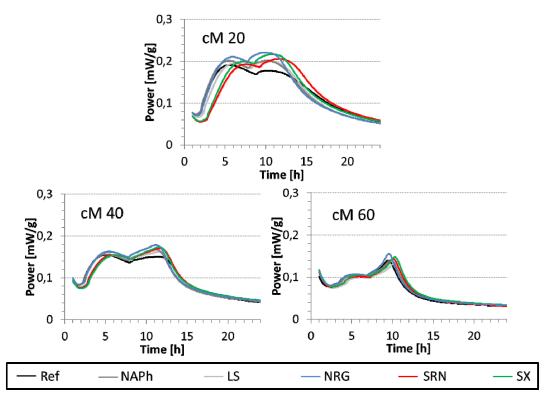

Figure 22. Rate of heat evolution of cement with 20, 40 nd 60 wt.% calcined marl containing 0.2 %bwob of different superplasticizers over a period of 24 h, prepared at a w/c ratio of 0.36
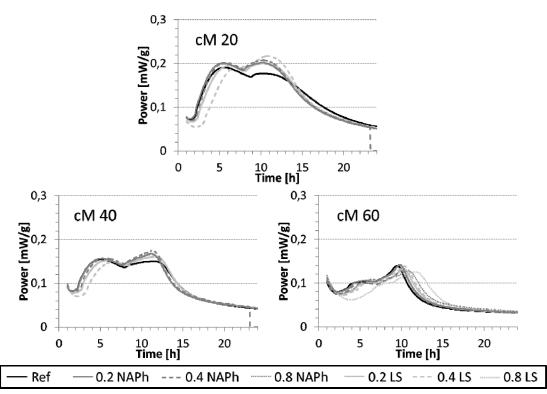
Figure 23. Rate of heat evolution of cement with 20, 40 and 60 wt.% calcined marl hydrated in the presence of 0.2 and 0.4 %bwob of NAPh or LS over a period of 24 h, prepared at a w/c ratio of 0.36. 0.8 %bwob of polymers were also employed for cements containing 60 wt.% calcined marl
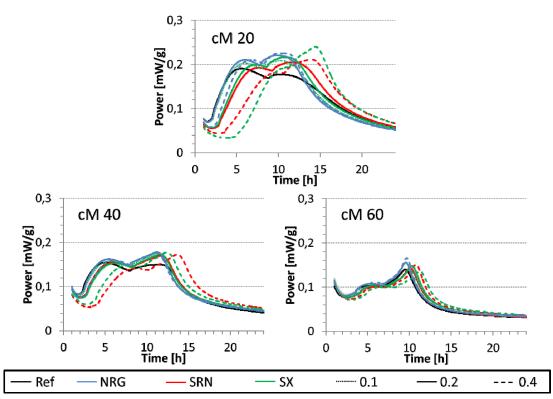

Figure 24. Rate of heat evolution of cement with 20, 40 and 60 wt.% calcined marl hydrated in the presence of 0.1, 0.2 and 0.4 %bwob of polycarboxylate based superplasticizers over a period of 24 h, prepared at a w/c ratio of 0.36

Table 28. Cumulative heat evolved of the cement slurries containing 20, 40 and 60 wt.% calcined marl in presence of superplasticizers, prepared at a w/c ratio of 0.36

Fly ash	Superplasticizer		Heat evolved$_{24h}$	Fly ash	Superplasticizer		Heat evolved$_{24h}$
[wt.%]	Type	[%bwob]	[J/g]	[wt.%]	Type	[%bwob]	[J/g]
20	NAPh	0.2	11.05	20	NAPh	0.4	10.96
20	LS	0.2	10.82	20	LS	0.4	10.62
20	SRN	0.2	11.02	20	SRN	0.4	10.60
20	SX	0.2	11.00	20	SX	0.4	10.30
20	NRG	0.2	11.32	20	NRG	0.4	11.14
40	NAPh	0.2	8.59	40	NAPh	0.4	8.59
40	LS	0.2	8.56	40	LS	0.4	8.29
40	SRN	0.2	8.74	40	SRN	0.4	8.40
40	SX	0.2	8.69	40	SX	0.4	8.51
40	NRG	0.2	8.92	40	NRG	0.4	8.72
60	NAPh	0.2	5.95	60	NAPh	0.4	5.64
60	LS	0.2	5.79	60	LS	0.4	5.99
60	SRN	0.2	5.85	60	SRN	0.4	6.15
60	SX	0.2	6.11	60	SX	0.4	6.15
60	NRG	0.2	6.03	60	NRG	0.4	6.20
60	NAPh	0.8	6.21	60	SX	0.1	5.86
60	LS	0.8	5.88	60	NRG	0.1	6.16
20	SX	0.1	11.18	40	SX	0.1	8.76

In the case of the addition of polycarboxylate superplasticizers, little retardation was observed up to an added dosage of 0.2 %bwob. However, upon addition of 0.4 %bwob (which was needed to ensure sufficient initial flowability of the cement for measurements) retardation of the cement pastes containing 20 and 40 wt.% calcined marl was observed as shown in Figure 24. This was however, not detected in cements containing 60 wt.% calcined marl. The observations here were in line with previous results. Therefore, it can be concluded that there is no significant impact of superplasticizers on the hydration profiles of cements containing calcined clay In spite of increased SP dosage relative to cement. This means that SP adsorbs more on calcined marl relative to fly ash.

4   Conclusion

In this report, the effectiveness of five different superplasticizers on two different blended cement systems at a w/c ratio of 0.36 was investigated. The five superplasticizers employed were a sodium lignosulfonate (LS) polymer, a polynaphthalene sulfonate polycondensate (NAPh), and three polycarboxylate based superplasticizers (NRG, SX and SRN) possessing varying charge densities and side chain lengths. The blended cements consist of a standard cement containing 20, 40 and 60 wt.% of either fly ash or calcined marl.

In general, addition of fly ash to the cement increased the fluidity of the cement pastes, while a reduction was observed when the cement clinkers were replaced with calcined marl. These findings can be explained by the dilution effect of relatively inert fly ash samples, thus increasing the availability of water in the system for improved rheological behaviour, while high sorption of water by the calcined marl accounted for the decreased in flow. In the case of cement pre-blended with fly ash (~20 wt.%) in the cement mill, the behaviour mimicked that of an ordinary Portland cement owning to the increased surface area designed to compensate for the lower FA reactivity by the producer.

In presence of superplasticizers, similar trend in the interactions of the blended cements with superplasticizers was observed relative to the ordinary Portland cement. The polycarboxylate based superplaticizers were more efficient in dispersing all cement systems than the naphthalene based and lignosulfonate. Additionally, the lignosulfonate superplasticizer was shown to increase the flow resistance of the cement pastes (decrease fluidity of the paste) with increasing dosages. Further elaboration for the different blended cement systems will be given below.

In the fly ash systems, the plasticizing effectiveness of the superplasticizers was as follow: NRG > SX > SRN > NAPH > LS, while the slump flow retention was SRN > SX > NRG > LS ≈ NAPh. Some interaction between fly ash and superplasticizers was detected but this was weak relative to that with cement clinkers and was shown to be reversible. Alike in the ordinary Portland cement system, NRG proved to be a very good plasticizer and no rheological measurements could be performed to a cement containing 60 wt.% fly ash when 0.2 %bwob of this polymer was added due to immediate segregation.

In the calcined marl systems, calcined marl was showed to compete with the cement clinkers for superplasticizers. The degree of competition varied according to the characteristic of the superplasticizers and SX, possessing an intermediate side chain length and charge density proved to be a much better dispersing agent here. The plasticizing effectiveness of the superplasticizers was SX > NRG > SRN > NAPh > LS, similar to an ordinary Portland cement or in the case of cement containing fly ash. The effectiveness of the dispersing agents on slump retention was SRN ≈ SX > NRG > LS > NAPh.

In the investigation of heat released during hydration of cements, pure fly ash showed negligible amount of heat released up to 24h. In cements containing fly ash, the cumulative hydration heat of the cements was reduced with increasing fly ash content, confirming the dilution effect of fly ash on the system. The trend in the effectiveness of superplasticizers (degree of retardation and change in total heat released) was similar to that observed in an ordinary Portland cement. Pre-blended fly ash cement displayed similar hydration profile as the ordinary Portland cement.

Pure calcined marl, on the other hand, displayed thrice the amount of heat released as that for a pure fly ash sample. This, in comparison to the heat evolved in cement hydration was however, negligible. When blended with cement, the calcined marl seems to contribute to the hydration of the cement paste (observe hydration profile of cement paste with 60 % calcined clay). In the case of calcined marl addition, no retardation was observed, up to a loading of

40 wt.% calcined marl. However, a replacement by 60 wt.% calcined marl displayed a change in hydration profile, indicating that hydration of calcined marl. Superplasticizers only affect and retard the hydration of the cement pastes at threshold superplasticizer dosages of 0.4 %bwob.

As a general outlook, further experiments such as GPC analysis of the adsorbed amount of superplasticizers can be performed. However, more importantly, two main areas can be pursued in our investigation. Firstly, due to the distinct characteristic of fly ash (filler and diluting effect) and calcined marl (hydrating and water adsorbing), a ternary cement blend of these two SCMs with cement clinker could be probed as a new binder material. In such a situation, the water retaining capacity of the calcined marl can be compensated by the fly ash, while the gain in initial strength of the paste can be covered by the calcined marl. It will be interesting to investigate the influence of superplasticizers on such a system.

Secondly, a deeper understanding of the effectiveness surface colloidal behavior of superplasticizers with the SCMs can be probed. This includes the difference in performance of the pre-blended system relative to the manually blended systems such as that compared here for the fly ash system. A better understanding of the surface chemistry between incoming superplasticizers and SCMs, and also the synergy effect in presence of the cement clinkers can form the foundations for the creation of new and more novel superplasticizers potentially targeting at the new generation of blended cements.

References

Cement Industry Energy and CO_2 Performance – "Getting the numbers right", World Business Council for Sustainable Development, The cement sustainability initiative (2011).

Cement Technology Roadmap 2009 – Carbon emissions reduction up to 2050, World Business Council for Sustainable Development (2009).

Chandra S., Björnström J., Influence of cement and superplasticizers type and dosage on the fluidity of cement mortars Part I, Cem. Concr. Res. (2002) 32, 1605–1611.

Habbaba A., Plank J., Surface Chemistry of Ground Granulated Blast Furnace Slag in Cement Pore solution and Its impact on the effectiveness of polycarboxylate Superplasticizers, J. Am. Ceram. Soc. (2012) 95, 768–775.

Kirby G.H., Lewis J.A., Comb polymer architecture effects on the rheological property evolution of concentrated cement suspensions J. Am. Ceram. Soc. (2004) 87, 1643–1652.

Lesti M., Ng S., Plank J., Ca^{2+} Ion – mediated interaction between microsilica and polycarboxylate comb polymers in model cement pore solution, J. Am. Ceram. Soc. (2010) 93, 3493 – 3498.

Mehta P.K., Concrete Technology for Sustainable Development, Concr. Internat. 21 (1999) 47-53.

M. M. Alonso, M. Palacios, F. Puertas, Compatibility between polycarboxylate-based admixtures and blended-cement pastes, Cem. Concr. Compos. (2013) 151–162.

Oss H.G.v., Cement – Annual Publication 2012, In: Mineral Commodity Summaries, Cement Statistics and Information, USGS - U.S. Geological Survey (2012).

The Global Cement Industry, Annual Review of Energy and Environment 26 (1002) 303–329.

Uchikawa H., Hanehara S., Sawaki D., The role of steric repulsive force in the dispersion of cement particles in fresh pastes prepared with organic admixtures (1997) Cem. Concr. Res. 27, 353–364.

World Cement Production (2011). European Cement Association (2012).

Worrel E., Price L., Martin N., Hendriks C., Meida L.O., Carbon Dioxide Emissions From

Zingg A., Winnefeld F., Holzer L., Pakusch J., Becker S., Figi R., Interaction of polycarboxylate-based superplasticizers with cements containing different C_3A amounts, Cem. Concr. Compos. (2009) 31, 153–162.

SINTEF Building and Infrastructure is the third largest building research institute in Europe. Our objective is to promote environmentally friendly, cost-effective products and solutions within the built environment. SINTEF Building and Infrastructure is Norway's leading provider of research-based knowledge to the construction sector. Through our activity in research and development, we have established a unique platform for disseminating knowledge throughout a large part of the construction industry.

COIN – Concrete Innovation Center is a Center for Research based Innovation (CRI) initiated by the Research Council of Norway. The vision of COIN is creation of more attractive concrete buildings and constructions. The primary goal is to fulfill this vision by bringing the development a major leap forward by long-term research in close alliances with the industry regarding advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

Technology for a better society

www.sintef.no