

Synthesis, Characterization, and Dispersing Performance of a Novel Cycloaliphatic Superplasticizer

by Lei Lei, Johanna de Reese, and Johann Plank

Synopsis: A novel superplasticizer made from cyclohexanone, formaldehyde and pyrosulfite utilizing a polycondensation reaction is presented. The new CFS polymer possesses a molecular weight of ~57 kDa and medium anionic charge density of ~1100 $\mu\text{eq/g}$. It disperses cements of diverse compositions (CEM I, CEM II, CEM III) effectively and does not retard cement hydration. In the presence of clay (montmorillonite), its dispersing performance is only slightly affected whereas that of a commercial polycarboxylate is severely perturbed. The reason behind is low adsorption of CFS on clay (~40 mg/g clay) while PCE sorbs in large quantity (~290 mg/g clay) and thus is deprived of cement. Adsorption and zeta potential measurements show that anionic CFS works by occupying positively charged surface sites on cement and achieves its dispersion effectiveness by instigating electrostatic repulsion between the cement particles.

Keywords: Cyclohexanone formaldehyde sulfite polycondensate (CFS); dispersion, adsorption, clay

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INTRODUCTION

Superplasticizers contribute an important class of admixtures which were invented in 1962.¹ Their advent has revolutionized modern concrete technology in that they allow to formulate concrete at very low water-to-cement (w/c) ratio such as for example 0.25, while maintaining good workability and pumpability. This way, a concrete possessing remarkably high strength (> 150 MPa) and excellent durability is attainable. Modern types of concrete such as self-compacting² or ultra-high strength concrete³ were made possible only through the use of these highly advanced superplasticizers.

Generally, superplasticizers can be categorized into four chemically distinctly different groups: (1) polycondensates; (2) polycarboxylates; (3) “small molecules”; and (4) biopolymers. Polycondensates were the first type of superplasticizer invented in 1962 independently by Aignesberger from SKW Trostberg, Germany and Hattori of Kao Corporation in Japan. Currently, β -naphthalenesulfonate formaldehyde (BNS) constitutes by far the major type of polycondensate-based superplasticizers used in concrete. Additionally, melamine-formaldehyde-sulfite (PMS),⁴ acetone-formaldehyde-sulfite (AFS)⁵ and sulfanilic acid-phenol-formaldehyde (SPF)⁶ polycondensates are applied as well. The chemical structures of currently available polycondensate superplasticizers are shown in Fig. 1.

Main advantages of polycondensate superplasticizers include robustness in performance which is less dependent on individual cement compositions and the presence of contaminants such as clays, and their relatively simple preparation from commonly available raw materials. Disadvantages of polycondensates are their poor slump loss behavior and the potential for residual free formaldehyde. In 1981, polycarboxylate ether (PCE) type superplasticizers were invented by Hirata at Nippon Shokubai in Japan.⁷ Here, for the first time, the concept of steric dispersion of cement was applied by designing comb polymers which possess lateral graft chains to provide the steric hindrance effect.⁸ Nowadays, a great diversity of polycarboxylate type superplasticizers is employed in concrete. Main advantages of PCE polymers include their highly tunable molecular structure, their superior performance at low w/c ratios (< 0.35) and – from polymers possessing high side chain density – excellent slump retention.⁹ For these and other reasons, PCEs have become very popular, and

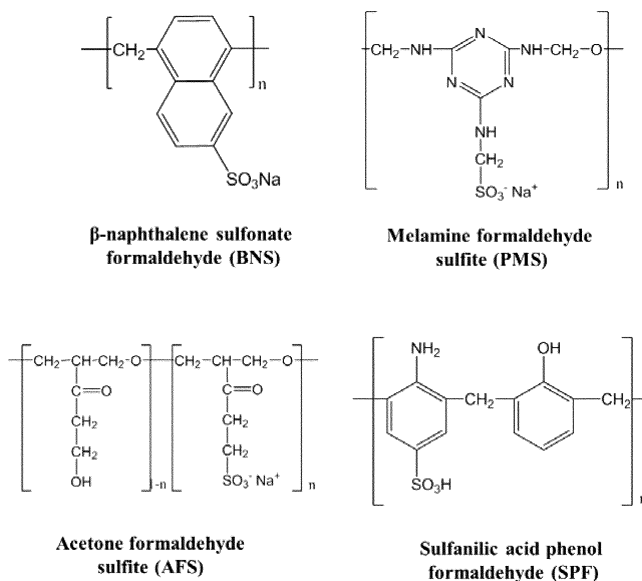


Fig. 1— Chemical composition of currently available polycondensate superplasticizers.

an estimated volume of 3 million tons has been used in 2010.¹⁰ Nevertheless, PCEs also exhibit some shortcomings which include: sensitivity to variations in cement compositions which can result in total failure to fluidify the concrete; this phenomenon is referred to as ‘cement incompatibility’ of some PCEs; sensitivity to clay contaminants contained in aggregates and limestone powder; it has been demonstrated that clays can sorb PCEs by chemical incorporation (intercalation) into their layer structure, thus screening off the polymer and depleting the amount which is available for cement dispersion.¹¹ The result is a huge loss in performance of PCE. Finally, PCE molecules are macro surfactants which can cause excessive foaming in concrete unless a suitable defoamer is applied.¹²

Recently, because of the above limitations of current PCE products, polycondensate superplasticizers have experienced a revival on the market. According to concrete manufacturers, the renewed interest is nourished from their reliable performance with different cement compositions and less foaming problems. Because of this trend, we have studied the possibilities for modification of polycondensate chemistry and hereby propose a novel type which is based on a cycloaliphatic ketone. At first, its synthesis from cyclohexanone, formaldehyde and pyrosulfite is described and its characteristic properties with respect to molar masses, molecular weight distribution and anionic charge density are presented. Next, employing a ‘mini slump’ test, its dispersing performance was tested with respect to dosage-dependent paste spread and maximum achievable water reduction. Different cements (CEM I, CEM II and CEM III) were employed to assess its robustness in actual concrete applications. Also, its tolerance to clay was probed by incorporation of 1% by weight of cement of sodium montmorillonite clay into the formulation. Finally, the working

Table 1—Phase composition of CEM I 42.5 R sample as determined by Q-XRD using *Rietveld* refinement

Phase	wt. %
C ₃ S, monoclinic	66.7
C ₂ S, monoclinic	15.0
C ₃ A, cubic	4.9
C ₃ A, orthorhombic	3.5
C ₄ AF, orthorhombic	2.3
CaSO ₄	1.9
CaSO ₄ ·1/2H ₂ O*	0.5
CaSO ₄ ·2H ₂ O*	0.5
Calcite	3.4
Quartz	0.8
Loss on ignition	1.8

*Determined by thermogravimetry.

mechanism of this novel superplasticizer was investigated by zeta potential and adsorption measurements.

RESEARCH SIGNIFICANCE

This paper describes a novel polycondensate type superplasticizer which can be made from versatile raw materials in a relatively simple synthesis. The new superplasticizer performs reliably with cements of diverse compositions including blended cements (CEM II/ CEM III). Therefore, it can enlarge the arsenal of superplasticizers available for specific applications, in particular for admixture formulations with high effectiveness in the presence of clay and silt contaminants..

EXPERIMENTAL PROCEDURES

Cement

For assessment of the general dispersing ability, the clay tolerance and the working mechanism of CFS, a CEM I 42.5 R (Heidelberg Cement ‘Milke classic,’ Geseke plant, Germany) was used. Its phase composition as determined by Q-XRD employing Rietveld refinement is presented in Table 1. The average particle size (d₅₀ value, determined by laser granulometry) was found at 11.08 μm and its *Blaine* fineness was 3 424 cm²/g (Helium pycnometry).

Compositions of the blended cements were as follows: CEM II/A-LL 42.5 R (Schwenk, Ulm, Allmendingen plant, Germany) 86.6% clinker, 2.2% anhydrite, 1.7% calcium sulfate hemihydrate, 1.2% gypsum and 8.3% limestone powder, d₅₀ value 12.75 μm, Blaine fineness 3610 cm²/g; CEM II B-V 42.5 R (Spenner, Erwitte, Germany) 72.5% clinker, 2.5% anhydrite and 25% coal fly ash, d₅₀ value 10.81 μm, Blaine fineness 3947 cm²/g; CEM III A 42.5 N (Schwenk, Ulm, Mergelstetten plant, Germany) 57.4% clinker, 1.3% anhydrite 1.2% calcium sulfate hemihydrate, 0.1% gypsum and 40% ground granulated blast furnace slag, d₅₀ value 8.89 μm, Blaine fineness 4 322 cm²/g.

Table 2—Oxide composition of Na⁺-montmorillonite sample as determined by X-ray fluorescence

Oxide	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	LOI	Total
wt. %	59.7	18.4	0.8	2.3	4.0	2.3	0.1	0.1	12.1	99.8

Clay

A commercial naturally occurring sodium montmorillonite clay sample (RXM 6020 supplied by Rockwood, Moosburg/Germany) was used as per obtained. Its oxide composition is presented in Table 2. It develops a pH of ~ 9 when prepared as a 2 wt. % aqueous suspension. Its *Blaine* fineness was 467,000 cm²/g (measured by BET).

Cycloaliphatic superplasticizer

The novel superplasticizer was synthesized from cyclohexanone, formaldehyde and pyrosulfite (molar ratio 1:3:0.25) employing an alkaline catalyzed aldol condensation reaction. Cyclohexanone (99% pure) and Na₂S₂O₅ (97% pure) were obtained from VWR International GmbH, Darmstadt/Germany. Formaldehyde (30 wt.% aqueous solution, methanol free) was purchased from Carl Roth GmbH + Co. KG, Karlsruhe/Germany. In a typical preparation, 0.125 mol of sodium pyrosulfite were dissolved completely in 150 mL of a 30 wt.% aqueous formaldehyde solution under vigorous stirring in a 1-L round-bottomed flask equipped with a reflux condenser and a thermometer. The pH value of the solution was adjusted to ~13 by addition of 31 mL of 30 wt.% aqueous NaOH solution. The solution warms to approximately 35°C and is kept at this temperature for 15 min. Next, 16 mL of isopropanol were added and cyclohexanone was fed in quickly. After about 1 minute, a strongly exothermic reaction occurs whereby the clear solution becomes yellow and starts to boil vigorously. The solution is heated to reflux for about 3 hours under constant stirring using an oil bath (120°C). During this time, the yellow solution changes to brownish and viscosity increases. Isopropanol is distilled off from the aqueous CFS solution (~ 45 wt.% concentration) which is cooled to ambient temperature and its pH value is adjusted to ~ 9 by addition of 80% formic acid. Complete incorporation of sulfite was tested by using Quantofix® test stripes (VWR International, Darmstadt, Germany). The resulting polycondensate solution exhibits a very light brownish color and a *Brookfield* viscosity (Model HA, equipped with spindle #3) of 160 mPa·s.

BNS

A commercial naphthalenesulfonate formaldehyde type superplasticizer from BASF SE, Ludwigshafen/Germany, a brownish powder was employed. Ion chromatographic analysis proved that the product was purified and contained less than 0.5 wt. % Na₂SO₄.

PCE

A commercial methacrylate (MPEG) type polycarboxylate from BASF SE, Ludwigshafen/Germany, a brown aqueous solution possessing a solid content of 20 wt.%, was used.

Characterization of superplasticizers

Molar masses (M_w , M_n), polydispersity index (PDI) and hydrodynamic radius ($R_{h(z)}$) of all superplasticizer samples were determined by size exclusion chromatography (SEC). Additionally, the anionic charge was measured.

Size exclusion chromatography was performed as follows: A solution containing 10 g/L of the polymer was prepared and applied on a Waters 2695 Separation Module equipped with three Ultrahydrogel™ columns (120, 250, 500) and a Ultrahydrogel™ guard column from Waters, Eschborn, Germany, and a subsequent 3 angle static light scattering detector (“mini Dawn” from Wyatt Technology Corp., Santa Barbara, CA). The polymer concentration was monitored with a differential refractive index detector (RI 2414, Waters, Eschborn, Germany). Aqueous 0.1 N NaNO_3 solution adjusted to pH 12 with NaOH was used as an eluent at a flow rate of 1.0 mL/min. The value of dn/dc used to calculate M_w and M_n was 0.195 mL/g (value for polystyrene sulfonate).¹³

Specific anionic charge densities of the polymers were determined utilizing particle charge detector PCD 03 pH (Mütek Analytic, Herrsching, Germany). This method allows the experimental determination of the anionic charge of polymers in solution. Here, 0.2 g/L of the polymers were dissolved in DI water or synthetic cement pore solution made from 1.72 g/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 6.959 g/L Na_2SO_4 , 4.757 g/L K_2SO_4 and 7.12 g/L KOH (pH value is 13.06) and were titrated against an aqueous 0.340 g/L solution of poly-diallyl dimethyl ammonium chloride (polyDADMAC) until charge neutralization (zero potential) was reached. From the amount of polyDADMAC consumed to reach a zero potential, the amount of negative charge per gram of polymer was calculated.

Performance test in cement

Performance of CFS in cement was tested by measuring paste flow, maximum water reduction achievable, and time dependent slump loss behavior.

A mini slump test according to DIN EN 1015 was utilized to determine paste flow as follows: First, the w/c ratio of the paste without polymer was set to give a spread of 18 ± 0.5 cm (7.1 ± 0.2 in.). At this w/c ratio, the dosages of polymers required to reach a spread of 26 ± 0.5 cm (10.2 ± 0.2 in.) were determined. Generally, the polymer was dissolved in the required amount of mixing water placed in a porcelain cup. When aqueous polymer solutions (CFS, PCE) were used, then the amount of water contained in the polymer solution was subtracted from the amount of mixing water. BNS powder was dissolved in the mixing water prior to cement addition. In a typical experiment, 300 g of cement were added within 60 sec to the mixing water and agitated with a spoon for 1 minute, then rested for 1 minute without stirring and were again stirred manually for 2 minutes using a spoon. After the stirring, the cement paste was immediately poured into a Vicat cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm; 1.57, 2.76 and 3.15 in. respectively) placed on a glass plate and the cone was vertically removed. The resulting spread of the paste was measured twice, the second measurement being in a 90° angle to the first and averaged to give the spread value.

Maximum water reduction achievable was tested as follows: First, the w/c ratio of the paste without polymer was set to produce a spread of 26 ± 0.5 cm (10.2 ± 0.2 in.). Next, different dosages of CFS were added and the w/c ratio at which the paste exhibits a spread of 26 ± 0.5 cm (10.2 ± 0.2 in.) was determined. The maximum water reduction achievable

with CFS was obtained when the w/c ratio could not be lowered any more despite further increases in CFS dosage.

Time dependent slump loss behavior was probed as follows: For the ‘mini slump’ test over time, 400 g of cement were mixed with the required amount of mixing water as described in the procedure above. After each measurement, the slurry was transferred back into the porcelain cup and covered with a wet towel in order to avoid drying. Before each subsequent measurement, the paste was manually stirred again for 2 minutes. Measurements were taken every 20 minutes and total period of the measurement was 240 minutes.

Behavior with clay

For the ‘mini slump’ test, pure cement was blended with 1% of clay (297 g cement, 3 g clay). This blend was mixed with the amount of mixing water required to obtain 26 cm (10.2 in) spread in the absence of clay, as described above. The water contained the dosage of superplasticizer needed to achieve 26 ± 0.5 cm (10.2 ± 0.2 in.) with the cement slurry holding no clay.

Working mechanism of CFS

Here, adsorption of CFS on cement and clay respectively, and the zeta potential of the cement paste were measured.

Adsorption was determined using the depletion method. The non-adsorbed portion of polymer remaining in solution at equilibrium was measured by analyzing the total organic content (TOC) of the solution. In a typical experiment, 16 g of cement, 8.8 g of DI water and the amount of superplasticizer to be tested were filled into a 50 mL centrifuge tube, shaken in a wobbler (VWR International, Darmstadt, Germany) for 2 minutes at 2400 rpm and then centrifuged for 10 minutes at 8,500 rpm. The supernatant was diluted with deionized water. Achievement of adsorption equilibrium was checked by comparing the adsorbed amounts found after one hour of stirring with values obtained after 2 minutes of exposure to cement. In both cases, the same values were obtained. The total organic carbon of the solution was determined by combustion at 890°C on a High TOC II instrument (Elementar Analysensysteme, Hanau, Germany). From the difference between the TOC content of the polymer reference sample and the TOC content of the supernatant, the adsorbed amount of superplasticizer was calculated. Measurements were generally repeated three times and the average was reported as adsorbed amount. Achievement of adsorption equilibrium was checked by comparing adsorbed amounts after one hour of stirring with values obtained after 2 minutes of stirring only. In both cases, the same values were obtained.

Sorption of polymer samples on clay alone in synthetic cement pore solution was performed employing solutions of concentrations between 12.5 to 150% by weight of (bwo) clay. These solutions were added to 0.02 g of clay, manually homogenized, sonicated for 10 minutes and centrifuged at 14,600 rpm for 10 minutes before TOC analysis. The $w/clay$ ratio was 55.

Zeta potential was determined using a model “DT 1200 Electro acoustic Spectrometer” (Dispersion Technology, Inc., Bedford Hills, NY, USA). This instrument measures a vibration current induced by an acoustic wave which causes the aqueous phase to move relative to the cement particles. From that, a potential difference results which can be measured and is designated as zeta potential. A 15 wt.% polymer solution was used for titration.

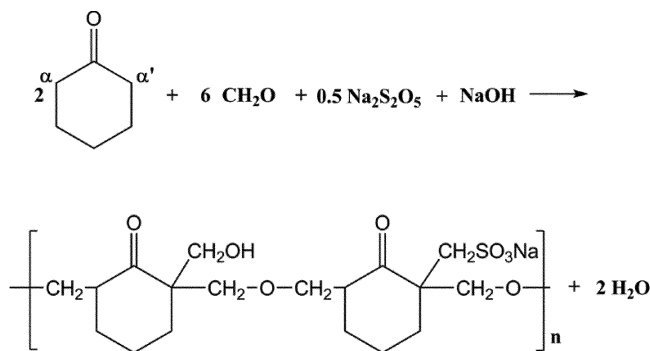


Fig. 2—Synthesis route and molecular structure of novel CFS superplasticizer.

EXPERIMENTAL RESULTS AND DISCUSSION

Synthesis and characterization of CFS

The novel CFS superplasticizer was synthesized from cyclohexanone, formaldehyde and sodium pyrosulfite at a molecular ratio of 1:3:0.25 using an aldol condensation process. There, under strongly alkaline conditions ($\text{pH} \geq 13$), cyclohexanone reacts with formaldehyde in α position to the ketone functionality by forming methylol groups. Subsequently, sulfite can react with one methylol group to form α -, α' -dimethylol α' -sulfomethyl cyclohexanone which then condensates to a linear polycondensate. The net reaction and molecular structure of CFS are shown in Fig. 2. Using this synthesis method, a yellowish or brownish, slightly viscous liquid with ~45 wt.% solid content is obtained. Its residual free formaldehyde content (Quantofix® test stripes, VWR, Darmstadt, Germany) was < 0.01 wt.%.

A difficulty in the synthesis of CFS is the relatively low solubility of cyclohexanone in the aqueous solution of $\text{Na}_2\text{S}_2\text{O}_5$. As a result, it reacts only slowly with formaldehyde, and a significant quantity (~30%) is left unreacted. To overcome this problem, isopropanol was found to act as a mutual solvent for cyclohexanone. It yields conversion rates of > 99% for cyclohexanone. Instead of isopropanol, also finished CFS solution can be used as mutual solvent in subsequent CFS preparations. The required amount was found to be similar to that of isopropanol.

The synthesized CFS polymer was characterized using SEC. From there, the molar masses (M_w , M_n), the polydispersity index (PDI) and the hydrodynamic radius ($R_{h(z)}$) of the solved macromolecule were obtained. Additionally, the same properties were determined for a CFS sample purified by dialysis, and for the commercial BNS and PCE samples. The results are shown in Table 3.

The data signify that the synthesized CFS still contains some impurities (oligomers, byproducts and residual starting materials). This effect is highlighted by the increased molecular weight of purified CFS which stems from the removal of low molecular and oligomeric by-products. The GPC spectrum of CFS purified by dialysis is presented in Fig. 3. It shows a strong signal representing a relatively uniform molecular weight distribution.

Table 3—Molar masses, polydispersity index (PDI) and hydrodynamic radius ($R_{h(z)}$) of synthesized CFS, purified CFS, and of commercial BNS and PCE samples

Polymer	M_w , g/mol	M_n , g/mol	PDI	$R_{h(z)}$, nm
CFS synthesized	27 330	10,900	2.5	7.8
CFS purified	57,090	43,300	1.3	4.3
BNS	139,100*	—	—	—
PCE	60,240	25,300	2.4	6.7

*Batch measurement.

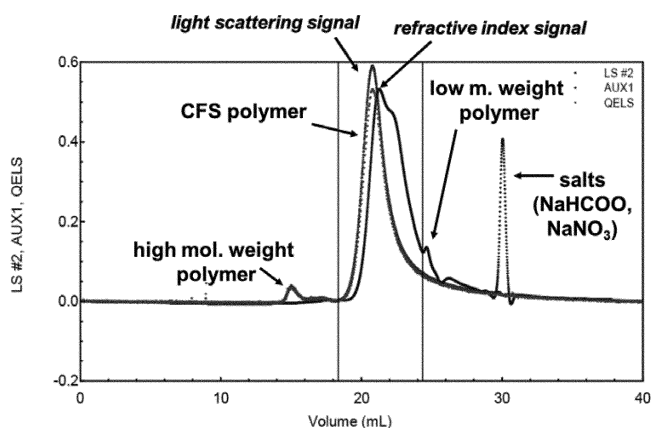


Fig. 3—Size exclusion chromatogram of CFS purified by dialysis.

of the polymer and a less intense signal for salts (Na^+ formate from pH adjustment and Na^+ nitrate from eluent). Additionally, two very weak peaks signifying low and high molecular weight species as by products are observed.

Next, anionic charge densities of synthesized and purified CFS, and of the commercial BNS and PCE samples were determined in DI water and synthetic cement pore solution, respectively. The results are exhibited in Table 4. Generally, the anionic charge of all samples tested was lower in cement pore solution than in DI water. This effect is ascribed to the chelating effect of Ca^{2+} ions present in cement pore solution. It shields some of the negative charge of the polyelectrolytes. CFS possesses a lower anionic charge than BNS. This was confirmed later by zeta potential measurements exhibited in Fig. 12. In future synthesis development, it should be attempted to increase the anionic charge of CFS by incorporating a higher amount of sulfonate groups, as it is expected to improve the dispersing performance of this superplasticizer.

Cement dispersing capacity

Effectiveness of CFS to disperse cement was probed using two different methods: (1) increase in paste flow as a function of CFS dosage and (2) maximum water reduction achievable with CFS.

Table 4 – Specific anionic charge amounts of superplasticizers tested

Fluid system	Specific anionic charge amount, $\mu\text{eq/g}$			
	Synthesized CFS	Purified CFS	BNS	PCE
DI water	1340	2980	4090	1055
Synthetic cement. pore solution	1100	2680	3910	351

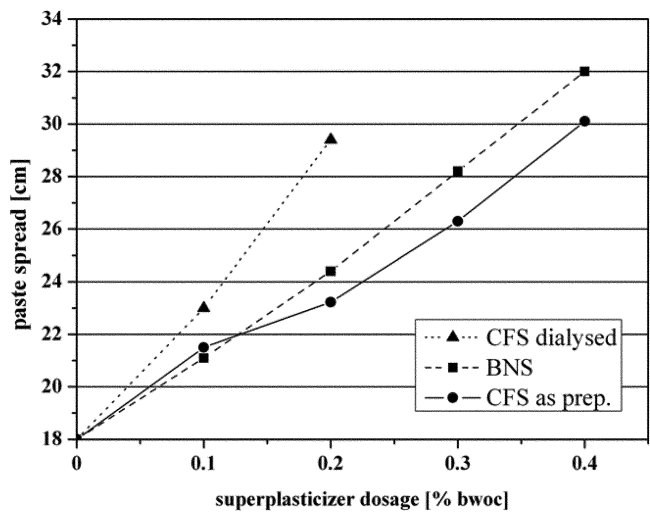


Fig. 4—Spread flow of cement pastes ($w/c = 0.55$) containing different dosages of CFS as prepared, of purified CFS and of commercial BNS sample. (Note: 1 mm = 0.039 in.).

“Mini slump” test

A paste prepared from CEM I 42.5 R at a w/c ratio of 0.55 which exhibited a spread of 18 ± 0.5 cm (7.1 ± 0.2 in.) was used as reference. As is shown in Fig. 4, CFS as prepared dispersed cement very effectively, but slightly less than the commercial BNS sample. The difference is owed to the fact that this BNS sample underwent a purification step in its manufacturing process whereby excessive Na_2SO_4 was removed. Consequently, compared to CFS, the BNS sample possesses a higher content of active polymer. This explains why the commercial BNS sample is slightly more effective than non-purified CFS obtained from the synthesis and used as is. Purified CFS even exhibited much superior performance over the commercial BNS sample, thus signifying the potential of this chemistry once its synthesis process is improved further to reduce inactive by-products.

Maximum water reduction achievable

Cement pastes (CEM I 42.5 R, w/c ratio 0.72, spread 26 ± 0.5 cm (10.2 ± 0.2 in.)) containing increased dosages of 0.1 – 1.2% bwoc of CFS or BNS were tested. At each dosage, the w/c ratio giving a spread of 26 ± 0.5 cm was determined and from this, the percentage of water reduction achieved was calculated. The results are shown in Fig. 5. Obviously, CFS possesses a high water reduction capability. For example, at a dosage of

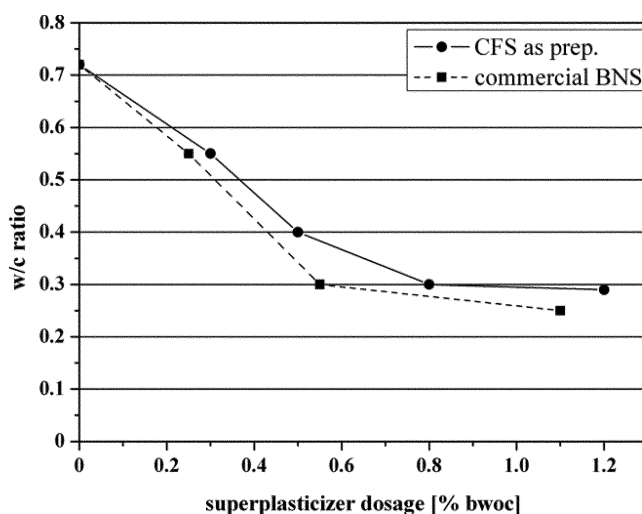


Fig. 5—Water reduction capability of CFS as prepared and of commercial BNS sample.

0.3% bwoc which is typical for actual application of polycondensates, the water reduction achieved was 24%. The maximum water reduction found for CFS was 60%, and the lowest w/c ratio attainable with this cement was 0.29 at 1.2% bwoc dosage. This compares with a w/c value of 0.25 for BNS which is superior over CFS, for the reasons explained above.

Time dependent slump loss behavior

The slump loss of a cement paste prepared at a w/c ratio of 0.55 and a CFS dosage of 0.3% bwoc corresponding to a paste flow of 26 ± 0.5 cm (10.2 ± 0.2 in.) was determined over a period of 4 hours. According to Fig. 6, the slump of this cement paste quickly decreased within the first hour, while it decreased slower afterwards. Such behavior is typical for polycondensate type superplasticizers.

Performance in blended cements

To assess effectiveness of CFS with blended cements, three CEM II/ CEM III samples were selected, a w/c ratio was set to achieve a spread of 18 ± 0.5 cm (7.1 ± 0.2 in.) and spread flows were measured at a fixed dosage of 0.3% bwoc of CFS. As is shown in Fig. 7, all blended cements produce lower fluidity with CFS than the CEM I 42.5 R sample. This effect is owed to the individual cement compositions. The data confirms that CFS is capable to disperse a diversity of different cements.

Impact of cement hydration

To detect a potential retarding effect of CFS, time-dependent heat evolution from CEM I paste (w/c ratio = 0.55) holding 0.3% bwoc of CFS and BNS was monitored. The results are exhibited in Fig. 8. There, it is demonstrated that, similar to BNS, CFS does not much influence the hydration kinetics of OPC. Particularly, no retardation was observed.

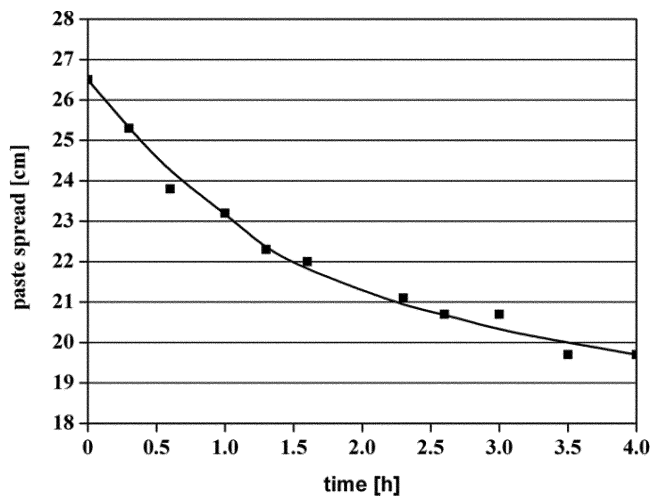


Fig. 6—Time-dependent paste spread (slump loss behavior) of a cement paste ($w/c = 0.55$) containing 0.3% bwoc of CFS as prepared (Note: 1 mm = 0.039 in.).

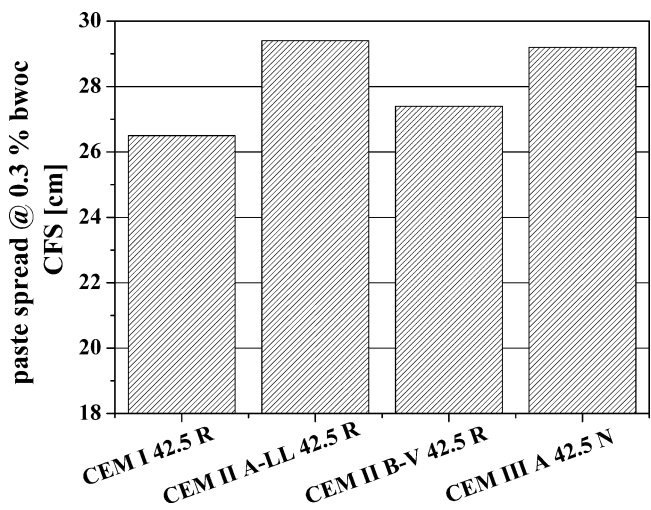


Fig. 7—Dispersing performance of CFS with blended cements (CEM II/III) in comparison to a CEM I sample. (Note: 1 mm = 0.039 in.).

Behavior of CFS in presence of clay

In this test, cement pastes prepared at a w/c ratio of 0.55 which exhibited a spread of 18 ± 0.5 cm (7.1 ± 0.2 in.) were used. 0.3% bwoc of CFS and 0.06% bwoc of PCE both gave a spread of 26 ± 0.5 cm (10.2 ± 0.2 in.) when added to this slurry. As is shown in Fig. 9,

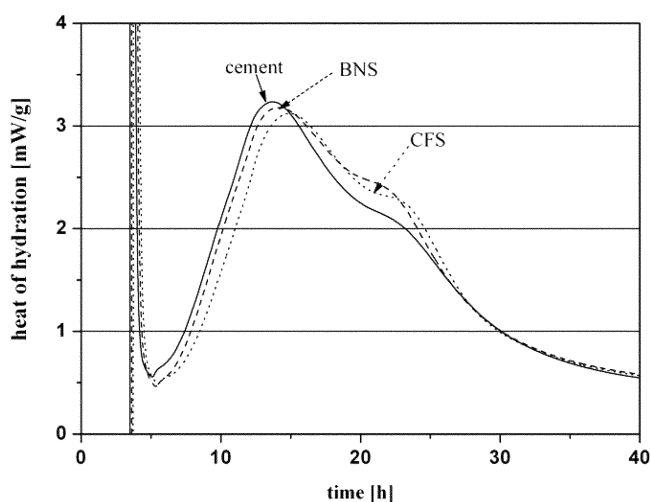


Fig. 8—Time-dependent heat evolution of CEM I 42.5 R paste ($w/c = 0.55$) containing 0.3% bwoc of CFS or BNS.

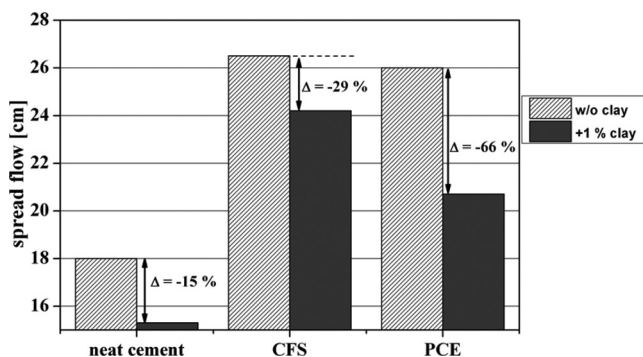


Fig. 9—Spread flow of cement paste ($w/c = 0.55$) holding 0.3% bwoc of CFS as prepared or 0.06% bwoc of PCE, measured in absence and presence of 1% bwoc of clay. (Note: 1 mm = 0.039 in.).

compared with PCE, CFS exhibited quite stable performance in the presence of 1% bwoc of Na^+ montmorillonite clay. The results demonstrate that CFS is more robust towards this type of clay than the PCE sample.

Interaction CFS—clay

To elucidate the reason behind the decreased impact of clay on CFS, its adsorption on montmorillonite suspended in synthetic cement pore solution was determined in comparison to that of BNS and PCE. The results are shown in Fig. 10. Obviously, CFS sorbs much less on clay (~10% only) than PCE which exhibits very strong interaction with this

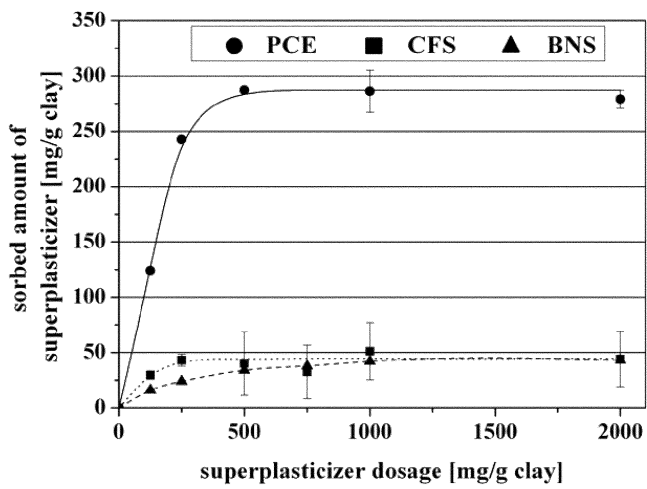


Fig. 10—Sorption isotherms of CFS as prepared, BNS and PCE on Na⁺ montmorillonite in synthetic cement pore solution (Ca^{2+} concentration = 0.4 g/L, w/clay = 55).

mineral. These differences in sorption behavior explain why CFS’s dispersing force is not much affected by clay. In contrast to this, PCE is virtually screened off from the pore solution by clay which then becomes so depleted of superplasticizer that cement dispersion is poor. Behavior of BNS was found to be comparable to that of CFS.

Working mechanism of CFS

The mode of action of the novel superplasticizer was probed via adsorption and zeta potential measurements.

Adsorption on cement

Figure 11 shows that CFS strongly adsorbs on cement, and that the adsorption isotherm is of *Langmuir* type. At low dosages, the adsorbed amount of CFS increases quickly and then gradually approaches a constant value of ~2.2 mg/g of cement, which represents the point of saturation adsorption. In comparison, BNS adsorbs in higher amount (~5.5 mg at saturation). This signifies that complete coverage of the surface of cement particles was achieved at a CFS concentration of ~0.8% bwoc. The results correspond well with the findings on water reduction capability displayed in Fig. 5. There, maximum water reduction was achieved at the same dosage of 0.8% bwoc. The results allow to conclude that CFS achieves cement dispersion by adsorption onto the cement surface, thus instigating a highly negative charge. Accordingly, the working mechanism of CFS at least in part is based on electrostatic repulsion of cement particles. Additionally, depending on the adsorbed conformation of CFS, steric hindrance may contribute to dispersion as well.

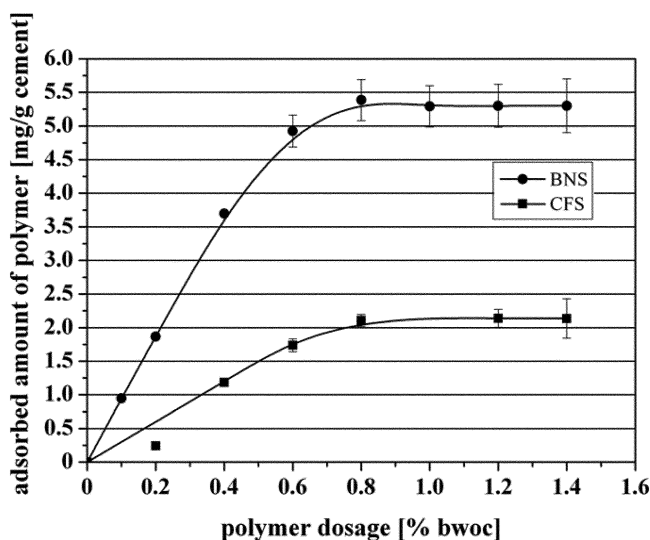


Fig. 11—Adsorption isotherms for CFS and BNS superplasticizers on CEM I 42.5 R ($w/c = 0.55$).

Zeta potential measurement

The electrostatic working mechanism was further probed by measuring the electrokinetic mobility of cement particles dispersed by increased dosages of CFS. The resulting zeta potential curve is shown in Fig. 12. In this test, aqueous CFS solution was titrated to a cement paste possessing a w/c ratio of 0.55. The zeta potential of the paste was measured at increasing CFS dosages of up to 2.2% bwoc. As shown in Fig. 12, at CFS dosages lower than 0.4% bwoc, the zeta potential which was -4.5 mV for the neat cement paste without CFS rapidly decreased to ~ -23 mV for the paste containing 0.4% bwoc of CFS. This signifies that adsorbed CFS instigates a highly negative charge onto the cement particles. Thus, occurrence of electrostatic repulsion between cement particles is confirmed. At CFS dosages above 0.4% bwoc, the zeta potential slightly decreased. This effect is characteristic for highly anionic polyelectrolytes and was described by other authors before.^{14,15} BNS shows a similar trend than CFS. The only difference is that, owed to its higher anionic charge, the suspension attains a more negative zeta potential (~ -31 mV) than in presence of CFS.

CONCLUSIONS

A CFS polycondensate was synthesized from cyclohexanone, formaldehyde and pyrosulfite as a ~ 45 wt.% aqueous solution using a simple process. CFS exhibits high water reduction capability ($\sim 60\%$), is effective at low w/c ratios (up to 0.29), is tolerant to diverse cement compositions including blended cements (CEM II/III), and shows robust performance even in the presence of clay. Although no particular effort was made to optimize its performance, already almost similar effectiveness than from a commercial purified BNS sample was attained. Thus, further improvement might be possible.

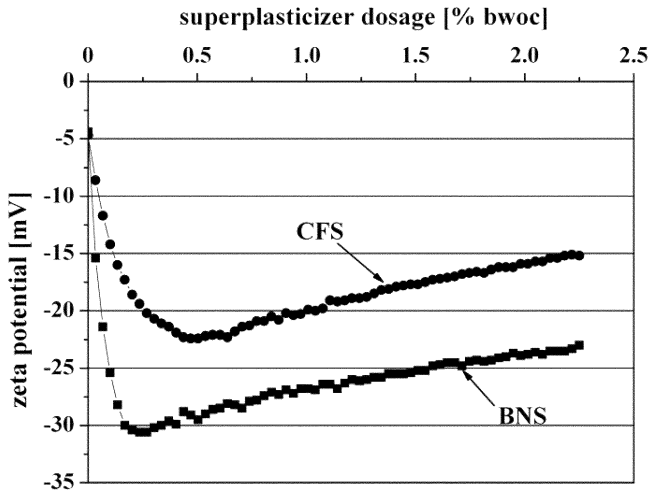


Fig. 12—Zeta potential of cement paste ($w/c = 0.55$) as a function of CFS and BNS dosage, respectively.

mechanism, CFS was found to behave like a typical polycondensate superplasticizer, i.e. it adsorbs on cement and induces a strong negative charge between cement particles. An attractive feature of CFS is its high tolerance to clays. Currently, the industry blends PCE solutions with polycondensate-based superplasticizers to mitigate the negative effects of clay on PCE. However, when using BNS, stability of the liquid blend can pose a problem. Because of its light color and less pronounced polarity, novel CFS might present another option to formulate more clay tolerant superplasticizer admixtures.

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Compatibility between Polycarboxylate and Viscosity-Modifying Admixtures in Cement Pastes

by Marta Palacios, Robert J. Flatt, Francisca Puertas,
and A. Sanchez-Herencia

Synopsis: Superplasticizers and viscosity-modifying admixtures (VMA) are often combined in the production of self-compacting concrete. The former provide high flow-ability and the latter are being increasingly used to enhance its stability. A deep knowledge of the mechanisms of action of both admixtures is needed for optimizing concrete design and for reducing possible technological problems on site.

The aim of the present study is to provide a scientific understanding of the compatibility between a PCE and two different VMA admixtures, starch and welan gum-based. For this, the interaction of both types of admixtures with cement was first studied by determining adsorption isotherms. Rheological tests were also performed and showed that the studied VMAs do not modify notably the plastic viscosity, but they control the stability of cement pastes by increasing the yield stress (up to 100%). Moreover, it was found that the increase of yield stress depends on the mode of VMA addition, reaching higher values when the VMA is added after the PCE.

Keywords: superplasticizers, viscosity-modifying admixtures, rheology, adsorption

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Javier Sanchez-Herencia is a specialist in colloidal and rheological optimization of slurries for processing of inorganic materials with complex microstructures. His interest is in study the employment of water compatible processing additives to make possible the fabrication of materials with both complex shapes and microstructures.

INTRODUCTION

Self-compacting concrete (SCC) is characterized by the ability to flow under its own weight, not requiring vibration during the placement process. The use of SCC involves economical, technical and environmental advantages, increasing quality of concrete and reducing global construction costs, timescales and noise level on construction sites. SCC is a complex system constituted by several components including one or more mineral additions and one or more chemical admixtures. A deep knowledge of the role of the different components in the SCC is needed to get the right composition that leads to its optima fresh and hardened properties.

Superplasticizers, and mainly polycarboxylate-based admixtures (PCEs), are essential in the preparation of SCC to reach high flowability with low water/cement ratio. These admixtures adsorb onto cement particles inducing their dispersion as a result of steric repulsion.¹⁻³ Additionally, SCC requires high amounts of fine powder materials, such as cement, fly ash, silica fume or limestone, to prevent segregation and bleeding during transportation and placing. However, over recent years, several studies have concluded to the possibility of alternatively using viscosity-modifying admixtures (VMA) to replace the fine powder materials in SSC, particularly in areas where these materials are not readily available.⁴

There are many organic and inorganic viscosity-modifying admixtures, such as cellulose, polysaccharides, polyethylene oxides or nanosilica. Their mode of action depends on their physico-chemical properties and dosage. VMAs were first presented as acting on plastic viscosity but several studies^{4,5} have confirmed they also increase yield stress. More

Table 1—Chemical composition (% weight) of portland cement

CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	SO ₃	Na ₂ O	K ₂ O	LOI	IR	Free CaO
58.84	21.70	4.87	2.23	3.72	3.46	0.76	1.63	1.21	0.48	1.10

Notes: LOI = Loss on ignition; IR = insoluble residue.

over, it is known that segregation tendency in a given mixture depends on the yield stress of the suspending Bingham fluid more than on its plastic viscosity.⁶ In the specific case of VMAs, it has also recently been suggested, that in cement paste without superplasticizers, the polyether cellulose VMAs act on yield stress by bridging flocculation. The same study could also account for the impact of modifications to the chemical structure of these polyethers.⁷ To the best of our knowledge, this is probably the only case where structure function relations of VMAs have been investigated by specifically including the role of the molecular structure.

Many investigations have been conducted to understand the interaction and compatibility of PCEs with cement.⁸⁻¹⁴ However, there are very few studies about the compatibility between PCEs and VMAs, which are very often simultaneously used in the preparation of SCCs. The main studies on this subject have shown for example that both type of admixtures are generally compatible.¹⁵ Others have indicated that specific combinations of superplasticizers and VMAs must be used.¹⁶ There is therefore still a large scope for further rationalization of the interactions between these admixtures. Consequently, the aim of the present study is to provide a scientific understanding of behavior and compatibility of PCE and VMA admixtures to avoid technological problems during the preparation and placement of SCC. For this, the interaction of both types of admixtures with cement has been studied via determination of the adsorption isotherms. Additionally, the effect of the admixtures on the rheological properties of cement pastes has been determined.

RESEARCH SIGNIFICANCE

Nowadays it has become a common practice to combine different chemical admixtures to improve at the same time several properties of concrete. This practice increases the risk of having problems on site due to the incompatibility between the admixtures such as quick loss of fluidity or high delay of hydration properties. In this paper, we deal with the combination of superplasticizers and VMAs, often used in the preparation of SCC. The understanding of the mechanism of action of both types of admixtures contributes to an improved and knowledge based designing of robust SCC mixes that can provide the best fresh and hardened state properties.

EXPERIMENTAL PROCEDURE

Materials

A commercial Portland cement CEM I 52.5N according to the European standard EN 197-1:2000 was used. Its chemical composition is shown in Table 1. Blaine surface area of the cement was 471 m²/Kg.

Table 2—Physical-chemistry characterization of commercial admixtures

Admixture	Superplasticizer	Viscosity modifiers	
	PCE	ST	WG
Solid content, %	39.0	7.0	4.1
pH	4.3	7.9	9.0
Mw (D)	27,000	2,000,000	80,000
% C	51.7	44.94	26.03
% H	8.0	7.33	3.72
% N	—	0.41	4.93
% S	0.3	0.02	17.99
% O	39.2	47.30	47.33

A commercial polycarboxylate-based (PCE) superplasticizer and two commercial viscosity-modifying admixtures, starch (ST) and welan gum-based (WG), were used. The physical-chemistry characterization of the admixtures is shown in Table 2.

Tests conducted

Adsorption curves of PCE and VMAs on cement

Twenty grams of cement and 40 g of distilled water containing PCE admixture were mixed and stirred for 30 minutes at 25°C to determine the adsorption isotherms for the superplasticizer.

The suspensions were subsequently centrifuged, the liquid phase was extracted off and the total organic carbon content was determined on a SHIMADZU TOC-VCSH/CSN total organic carbon (TOC) analyzer. Admixture adsorption by the cements studied was taken to be the difference between the amount initially added and the amount present in the liquid phase measured by TOC.

The adsorption isotherms of starch- and welan gum-based VMAs on cement were determined using the same methodology.

Rheological behavior

Cement pastes with a liquid/solid ratio of 0.4 were prepared by mixing at 150 rpm for 3 minutes with a blade stirrer. A dosage of 1 mg PCE/g cement was incorporated. Additionally, a dosage of VMA in the range between 0 and 0.7 mg VMA/g cement was added.

To understand the mechanism of action of PCE and VMA admixtures, two different addition modes of the VMA were studied: (a) VMA was added at the same time than the PCE with the mixing water and (b) VMA was added after one minute of mixing of water and PCE with cement.

Cement pastes rheology was measured with a controlled shear rate Haake RV20 rotational viscometer by using an M5 measurement system with a coaxial cylinder MV2 rotor. The method used lasted 32 minutes and it consists in a shear rate continuous ramp from 0 to 400 s⁻¹ over 16 minutes followed by a steady step of 1 minute at 400 s⁻¹ and a final reversed ramp from 400 s⁻¹ to 0 s⁻¹ over 16 minutes. Each rheological test was repeated three times.

Cement paste flow tests

Cement pastes with liquid/solid ratio of 0.4 were prepared using the same protocol as in the rheological tests. In addition, a dosage of 1 mg PCE/g cement was incorporated and a dosage of 0.21 mg VMA/g cement was added in the two different ways previously described.

After mixing, the paste is filled in a cylinder of 50 mm of diameter and 50 mm height. The cylinder was lifted and the diameter of the resulting cake was measured as a flow value. Flow values were also determined after 15 min, 30 min and 60 min. In these cases, paste was previously remixed during 30 seconds in the blade stirrer.

The flow spread can be linked to the yield stress according to the Eq. (1).¹⁷ As all the measured flow spreads are lower than 220 mm, the surface tension effect can be neglected.¹⁷

$$\tau_0 = \frac{225\rho g V^2}{(128\pi^2 R^5 (1 + \frac{225}{128\pi} \sqrt{3}VR^{-3}))} \quad (1)$$

where ρ and V are the density and volume of the paste, respectively; g the gravitational acceleration; and R the radius of the spread.

RESULTS

Adsorption curves of PCE and VMAs on cement

Figure 1 shows the adsorption isotherms of the superplasticizer (PCE) and of both organic VMA admixtures on Portland cement. For the PCE, the adsorption is linear at concentrations up to 1mg PCE/g cement, being progressive adsorbed at higher concentrations.

Figure 1 also confirms the adsorption of the VMA admixtures on cement. The plateau value for starch-based VMA adsorption is slightly lower than the PCE; however, for the welan gum-based VMA admixture, the adsorption is linear up to 12 mg WG initial/g cement and the plateau value is close to 10 mg WG adsorbed /g cement (around 10 times higher than PCE polymer).

In the range of VMA dosage used in the rheological tests in the present study—0 to 0.7 mg VMA/g cement—the adsorption of PCE and welan gum-based admixtures on cement (see Fig. 1(b)) is very similar, however, the affinity of starch is lower by 37%.

Rheological behavior

Figure 2 shows an example of the flow curves for all the studied cement pastes with and without the VMA where it can be clearly observed that all pastes present a thixotropic loop.

Figure 3 shows the evolution of the apparent viscosity during the increase of shear rate. The addition of both VMAs to the cement pastes increases their shear thinning. This behavior becomes more pronounced as the dosage of VMA is increased. Moreover, of the two VMAs, it is the starch-based one that leads to the most pronounced shear thinning behavior.

For starch-based VMA, its addition mode has a significant influence on the increase of the apparent viscosity. More specifically, adding the superplasticizer first and the VMA

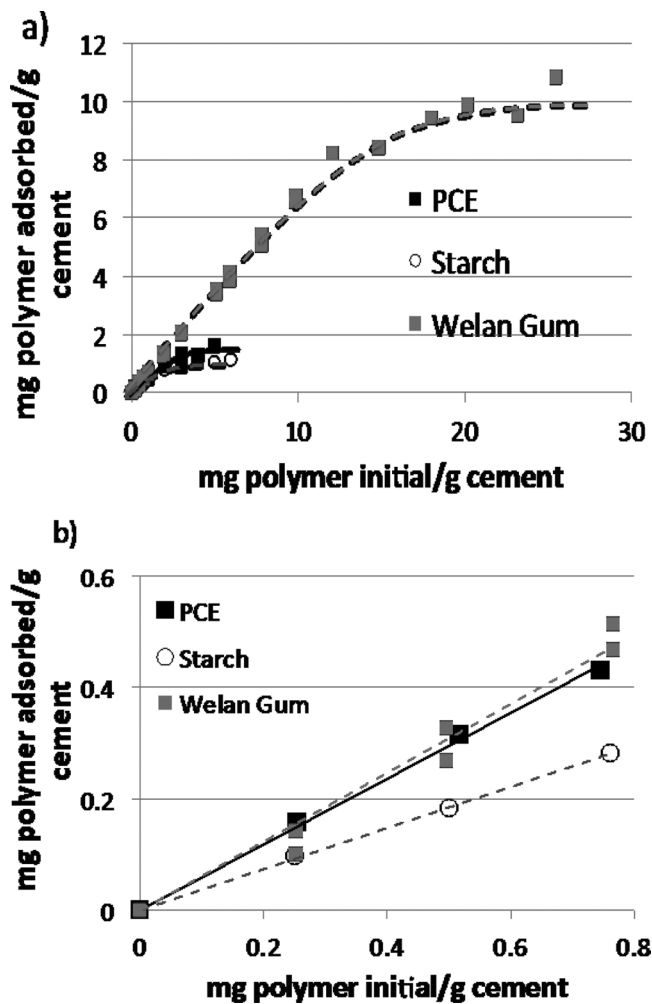


Fig. 1—Adsorption isotherms of PCE, ST and WG admixtures on cement suspensions.

later leads to a higher increase of apparent viscosity than when both admixtures are added simultaneously. On the contrary, the mode of addition of welan gum-based VMA does not significantly influence the apparent viscosity.

The flow curves obtained while decreasing shear rate were also analyzed. In all cases, they were fitted to a straight line according to the Bingham equation (see Eq. (2))

$$\tau = \tau_0 + \mu \dot{\gamma} \tag{2}$$

where τ_0 is the yield stress and μ the plastic viscosity.

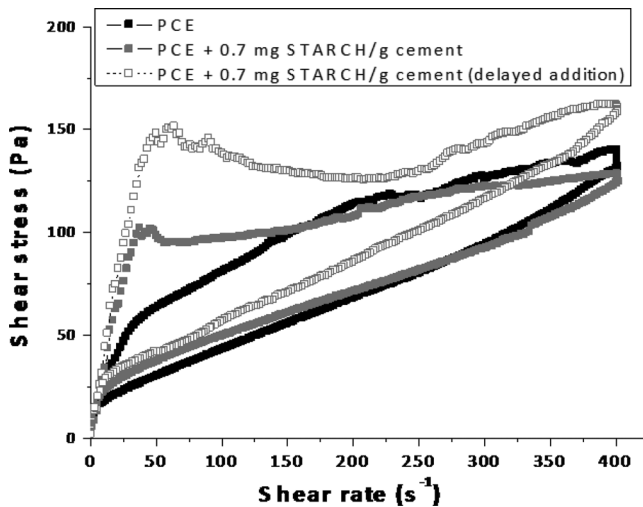


Fig. 2—Example of hysteresis cycles of the studied cement pastes with and without the VMA.

The dependence of the yield stress with the dosage, type of admixture and addition mode is shown in Fig. 4(a) and (b). From this, it can be seen that the addition of both VMAs increases the yield stress more as the amount of VMA increases. In addition yield stresses are higher when starch-based VMA is added. Specifically, a dosage of only 0.21mg ST/g cement increases the yield stress by 75%, while 0.7mg/g cement of welan gum are needed for the same effect. For both VMAs, their delayed addition leads to higher yield stress values.

Finally, none of the VMAs studied increases the plastic viscosity of cement pastes with the exception of the delayed addition of ST-VMA at dosages higher than 0.21mg ST/g cement (see Fig. 4 (c) and (d)).

Cement paste flow tests

Results shown in Fig. 5 confirm that both VMAs reduce the flow spread and consequently increase yield stress. These changes are significantly larger in pastes containing starch-based admixtures rather than welan gum-based ones, which is fully compatible as expected with what was observed in the rheometer tests. The same trends in terms of admixture dosage and addition time are also found both in the rheometer and in the flow spread measurements (in terms of yield stress). Apart from this, it can be noted from the flow measurements that yield stress does not evolve much over time in these suspensions.

DISCUSSION

In self-compacting concrete several admixtures are combined to control its rheological properties, superplasticizers provide high flowability and viscosity-modifying admixtures (VMA) are being increasingly used to enhance its stability.

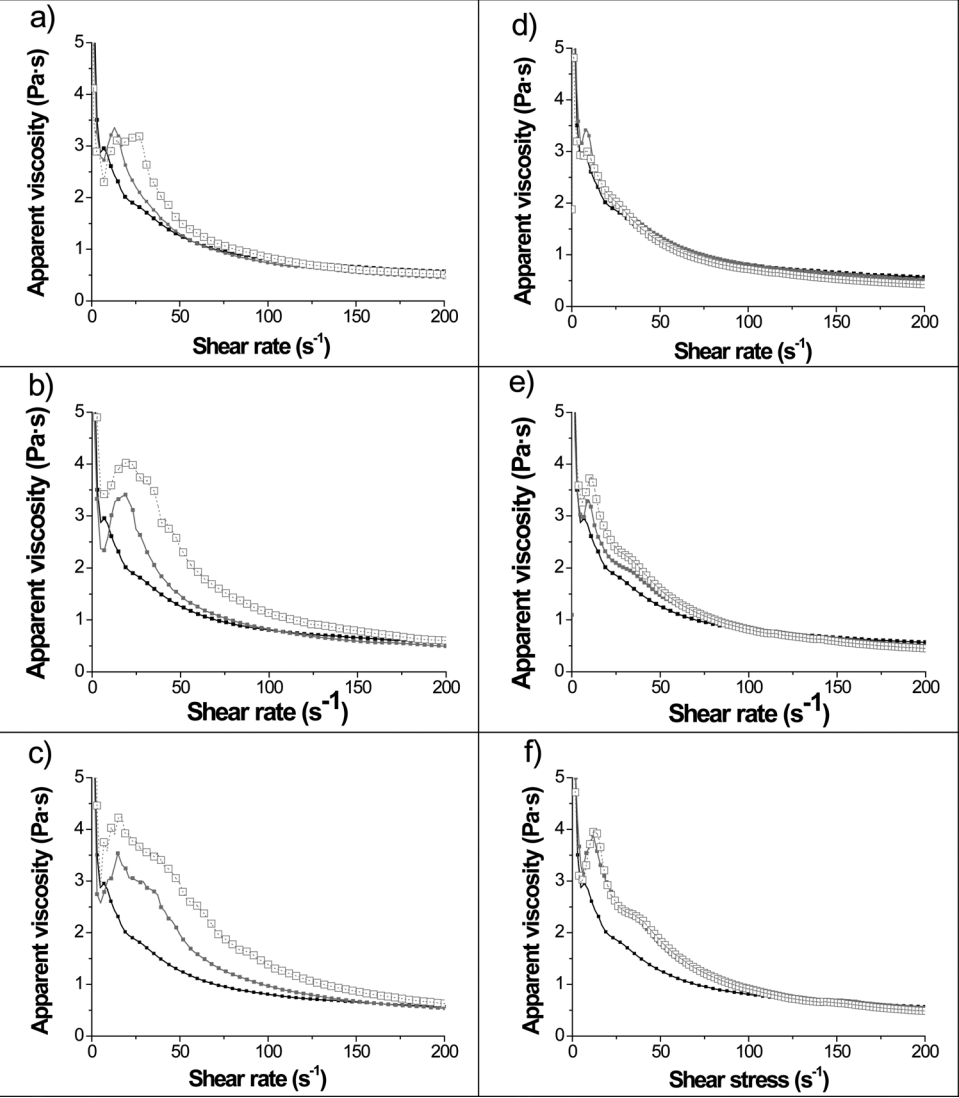


Fig. 3—Evolution of the apparent viscosity of cement pastes with starch-based VMA (a,b,c) and welan gum-based VMA (d,e,f) for dosages of 0.21 mg/g (a,b), 0.42 mg/g (d,e) and 0.70 mg/g (c,f). Black, gray, and open symbols correspond to no VMA, VMA in direct addition and VMA in delayed addition, respectively.

The rheological results presented, at constant dosage of PCE, add to the growing evidence that the addition of starch- and welan gum-based VMAs does not modify notably the plastic viscosity, but controls the stability of cement pastes by increasing their yield stress (up to 100%) (see Fig. 6). The yield stress increases with higher dosages of VMA to an extent that clearly depends on the VMA mode of addition, reaching the greatest yield

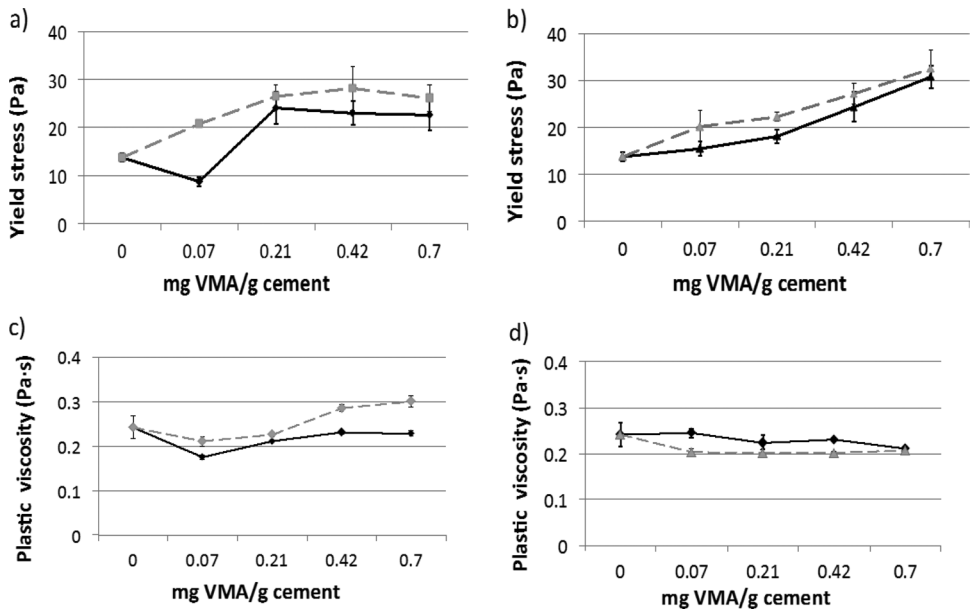


Fig. 4—Evolution of the yield stress and plastic viscosity of cement pastes with 1 mg PCE/g cement and (a,c) starch-based VMA and welan gum-based VMA (b,d). Black and gray symbols are, respectively, for direct and delayed addition.

stresses when the VMA is added after the PCE. Moreover, the two VMAs behave quite differently. Indeed, the yield stress increases linearly with dosage for the welan gum, while it seems to reach a plateau with the starch based VMA.

To understand these differences, we must examine the possible mechanisms at play. First of all, concerning the PCE present in all our mixes, we recall that it works by adsorbing onto cement particles to induce a steric repulsion that decreases yield stress.² Electrostatic forces, possibly mitigated by calcium ions, drive the adsorption of PCEs.

The VMAs used in this study have much larger molecular weights than PCEs. They physically adsorb large amounts of water by hydrogen bonds, increasing their effective volume and consequently the viscosity of the interstitial fluid of cementitious systems.^{18,19} This increase is however much larger than that of the high shear viscosity of cement pastes.⁷ Apart from this specific effect on the continuous phase, VMAs can also adsorb onto cement particles (see Fig. 1 or References 18 and 20).

In the case of cellulose ethers, in absence of PCEs, this adsorption has been shown to be responsible for an increase in yield stress because of bridging flocculation.⁷ If this were also true on our systems, one would expect welan gum, the most adsorbing VMA polymer (Fig. 1(b)), to increase yield stress most. However, Fig. 5(b) shows that the opposite is true. This suggests that non-adsorbed polymers may be responsible for the yield stress increase in presence of PCEs.

In support of this, we can note that VMA delayed addition increases yield stress (Fig. 4(b) and Fig. 3(a) and (b); differences probably coming from shear history). This effect

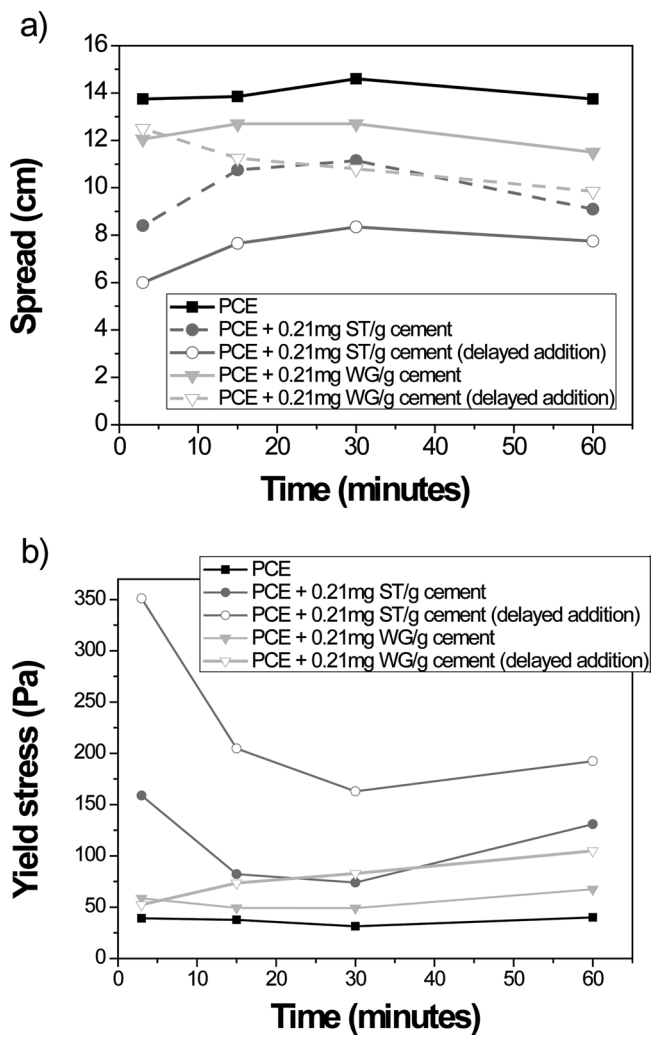


Fig. 5—Flow test results and calculated yield stress of cement pastes with addition of PCE and VMA.

of addition time may mean that PCEs prevent the VMAs from adsorbing if they reach the surface first (first come first serve). Therefore a delayed addition would increase the amount of non-adsorbed VMAs, supporting again the role of non-adsorbed polymers in increasing yield stress.

The mechanism in questions would be depletion flocculation. It occurs because non-adsorbed polymers are depleted from a “volume exclusion shell” around larger particles and that this excluded volume decreases when those particles flocculate due to the overlap of their “volume exclusion shells”²¹.

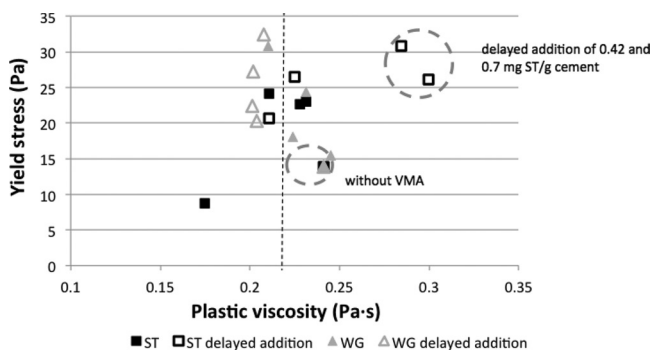


Fig. 6—Yield stress versus plastic viscosity of admixed cement pastes.

Depletion flocculation is proportional to the molecular weight of the polymer,²² which might explain the higher yield stress induced by starch-based VMA with respect to welan-gum. However, this depends also of the molar mass of the characteristic repeat lengths that are different between welan gum and starch. Depletion flocculation also increases with the concentration of non-adsorbed polymers.¹⁸ However, as we are assuming that PCE dominates the adsorption, the depletion force between two particles should be proportional to the VMA dosage. In further support of this, let us recall that the PCE dosage is selected to allow reaching a complete surface coverage, based on the adsorption isotherm (Fig. 1). At lower PCE dosages, in contrast to this study, cross-flocculation may not be negligible.

The depletion force also depends on the separation distance between particles.¹⁸ This is probably not modified by VMAs as this distance is probably on the order of twice the adsorbed layer thickness of PCEs. Indeed, steric hindrance increases very strongly with overlap so that we do not expect the different VMAs to produce substantial compressions of those adsorbed layers.

We now can state that the depletion force between particles is probably proportional both to the molar mass and to the dosage of the VMA.¹⁸ We now need to relate this interparticle force to the yield stress. At a fixed volume fraction, we can assume that the yield stress will be proportional to the interparticle force.²³⁻²⁵ Consequently, we expect the yield stress of cement suspensions to increase linearly with the VMA dosage. This is clearly the case with welan gum (Fig. 4(b)), which tends to support the role of depletion flocculation. For starch, it may be the case at the lowest dosages used (Fig. 4(a)).

The fact that a yield stress plateau is reached as the starch dosage is increased may be linked with the higher molecular weight, from a critical micelle concentration or a solubility limit present for starch at these concentrations but not for welan gum. Such a hypothesis would also need to be examined in future work.

Further studies are needed to confirm the depletion flocculation mechanism formulated in the present work. Specifically, measuring the adsorption of VMA in cement pastes containing PCE should provide more conclusive results. They should in particular define the importance of competitive adsorption between these admixtures, something that could not be addressed with the present data. In addition, the determination of depletion forces

by AFM might give the whole picture of the forces induced by both VMAs in cementitious systems.

CONCLUSIONS

We have studied the rheological behavior of cement suspensions contained VMA at variable dosages in addition to a PCE at a dosage sufficient to reach surface saturation. Under these conditions, it was found that neither starch- or welan gum-based VMAs significantly modify the plastic viscosity, while they both increase yield stress. This effect increases with higher dosages of VMA and it clearly depends on the VMA mode of addition, reaching the greatest yield stress values when VMA is added after PCE incorporation. This increase in yield stress should be seen as the reason for the stabilization that VMAs offer against segregation.

This stabilization induced by both VMAs could be due to a depletion flocculation mechanism. This mechanism would explain the increase of the yield stress of cement pastes as the amount of VMA in the interstitial fluid increases. Depletion flocculation is proportional to the molecular weight of the polymer, what might explain the higher yield stress induced by starch-based VMA with respect to welan-gum. More importantly it seems to account for the linear increase of yield stress with the dosage of welan-gum.

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Aspects of Gypsum-Free Portland Cement

by Harald Justnes

Synopsis: Calcium sulphate (e.g. gypsum) is the common set regulator in portland cement. It has been shown that ground calcium sulphate (e.g. gypsum) is the common set regulator in portland cement. It has been shown that ground clinker can be set regulated by other calcium salts than gypsum, in particular calcium acetate, formate, and nitrate. Rheology of paste is improved when gypsum is replaced by the other salts, probably due to less water binding and less needle shaped surface hydration products than ettringite. For in particular calcium nitrate the cumulative hydration temperature is reduced, which opens up for low-energy cement without changing clinker chemistry. Removing calcium sulphate all together may also allow heat curing or evolution of hydration heat in massive structures to exceed 70°C (158°F) without risking delayed ettringite formation (DEF). These aspects have been elucidated by experiments in the present paper.

Keywords: calcium acetate; calcium formate; calcium nitrate; chemical admixture; gypsum; low energy cement; delayed ettringite formation; rheology.

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INTRODUCTION

Portland cement is Portland clinker interground with calcium sulphate mainly as set retarder for C_3A forming an initial layer of ettringite,¹ even though it is also known that sulphates accelerates the hydration rate of alite² and partly counteracts early shrinkage by the ettringite formation in reaction with C_3A . Calcium formate³ and calcium nitrate⁴ are commonly used in Portland cement (i.e. with calcium sulphate) as accelerators, but no reports have been found on the effect of such calcium salts on Portland cement clinker without calcium sulphate. This paper shows some initial results where this is the case and discusses the potential implications that may arise from the changes in properties.

RESEARCH SIGNIFICANCE

Replacing calcium sulphate with other calcium salts as setting regulator in Portland cement may imply:

1. Less water demand for equal rheology due to no ettringite formation in the fresh state.
2. Calcium nitrate replacing gypsum leading to less heat of hydration first 24 h means that low-energy cement can be produced without changing clinker chemistry.
3. No gypsum in the system can open up for heat curing above 70°C (158°F) improving productivity in element production, or allowing temperature increase above 70°C (158°F) in massive structures removing need for cooling, without risking delayed ettringite formation (DEF) leading to later expansion and cracking.

EXPERIMENTAL INVESTIGATION

Materials

The compositions of the two Portland clinker used as analyzed by XRF are given in Table 1, while the potential minerals according to Bogue calculations and actual minerals as determined by Rietveld analyses of XRD profiles for clinker 1,⁵ and as received from the producer for clinker 2, are listed in Table 2. The Blaine of the clinker 1 was 450 m²/kg (327,000 in²/lb) while loss on ignition (LOI) was 0.3%. Clinker 1 was obtained from the Norwegian cement plant of Norcem in Brevik, while clinker 2 was obtained from Heidelberg cement research center in Leimen, Germany.

Laboratory grade gypsum, calcium formate and calcium acetate were used in the study, while 50% solution of calcium nitrate was delivered by the Norwegian company Yara International. Distilled water was used for pastes, while tap water purified by ion exchange was used for mortar.

Table 1—Oxide composition of portland clinkers by XRF

Oxide	Content (%) Clinker 1	Content (%) Clinker 2
CaO	60.6	67.6
SiO ₂	20.0	23.4
Al ₂ O ₃	5.4	4.0
Fe ₂ O ₃	3.1	1.5
MgO	2.9	0.7
SO ₃	1.5	0.4
P ₂ O ₅	0.1	0.2
K ₂ O	1.2	0.7
Na ₂ O	0.5	0.2
Free CaO	1.85	—

Table 2—Mineral composition of clinkers determined by Bogue and Rietveld analyses

Minerals	Bogue (%) Clinker 1	Rietveld (%) Clinker 1	Bogue (%) Clinker 2	Rietveld (%) Clinker 2
C ₃ S	54.0	54	68.2	74.2
α -C ₂ S				5.9
β -C ₂ S				7.7
Total C ₂ S	16.6	19	15.7	13.6
Cubic C ₃ A				3.6
Orthorhombic C ₃ A				5.9
Total C ₃ A	9.1	11	8.2	9.6
C ₄ AF	9.4	8	4.4	2.3

Specimens

Clinker 1 pastes (300 mL) were made by distilled water to $w/c = 0.40$. 3.5% gypsum of clinker mass (dosage according to corresponding commercial cement) was dry blended before water was added, while 2% of the other calcium salts (minimum safe dosage required according to avoid flash set tested in 0.5% increments) by clinker mass were dissolved in the water before addition to the clinker. The pastes were prepared in a MR5550CA high shear mixer of Braun. They were blended for 1 minute, resting for 5 minutes and mixed once more for 1 minute to stir up any false set.

The stepping up and down flow curves of the pastes were recorded by a rheometer MCR

300 by Physica starting from shear rate ($\dot{\gamma}$) 1 s^{-1} to 150 s^{-1} and immediately down again. This was repeated regularly from 10 to 90 minutes after resting with stirring up at 100 $1/s$ for 1 minute in between. A parallel plate setup was used with a $1 \text{ }\mu\text{m}$ (0.040 in.) gap and both upper and lower plate serrated to a depth of 150 μm (0.006 in.). The paste with gypsum and calcium nitrate had identical program, while calcium acetate and formate was measured one more time within the interval. Linear fitting of the downwards flow curve

was done for the linear part from $\dot{\gamma}$ 99 to 43 s⁻¹ resulting in the Bingham viscosity from the slope and yield point from the intercept with the ordinate axis.

The isothermal calorimetry of the same pastes as for the rheology tests were measured by a TAM air calorimeter as rate of heat evolution as well as cumulative heat. The paste samples were accurately weighed to about 6 g (0.013 lb) into glass vials and sealed before they were placed in the different channels in the calorimeter.

Mortars were made according to EN 196-1 for clinker 1 with 3.5% gypsum and with 2% calcium nitrate. Two 160 x 40 x 40 mm (6.3 x 1.6 x 1.6 in.) prisms sets of 3 parallels were cast for each mix, and one of the sets had cast in studs at the ends for length measurements. The spread of the mortars were measured immediately after mixing as well as just after casting the first set. One set was used to measure the 1 day strength after curing at 20°C (68°F) in the mold, while the set with studs was demolded and placed in a container with water that subsequently was placed in a room of 80°C (176°F) for 3 days before it was again placed in a 20°C (68°F) room and allowed to cool to ambient for further storage. Thereafter the lengths of the individual prisms were registered and the length change monitored monthly to see if there were any difference in expansion due to e.g. delayed ettringite formation (DEF).

Clinker 2 was used for larger batches of mortars where 3% gypsum (estimated due to less C₃A content than in clinker 1) or 2% calcium nitrate was added. Ten liters (610 in.³ [0.35 ft³]) of mortar were contained in a plastic bag inside a box with 150 mm (5.9 in. [0.49 ft]) Styrofoam walls in order to simulate the situation in a massive structure and the conditions can be characterized as semi-adiabatic. The box was placed in a 38°C room in order to further minimize heat loss. The temperature was logged in both mortars in order to see the difference in maximum temperature. Unfortunately the thermocouple in the mortar with gypsum failed just after working hours and re-established next day, but the maximum temperature was missed. The mortar with calcium nitrate reached 84°C (183°F), and due to the steepness in temperature rise it is assumed that the mortar with gypsum reached even higher. Five days later both mortar blocks were demolded and stored under water at 20°C (68°F). In order to utilize the mortar blocks they will be weighed above and under water monthly in order to monitor the change in volume by DEF according to Archimedes principle. The same mortars were filled in three pieces of double 100 mm (3.9 in.) cubic Styrofoam molds with 20 mm (0.79 in.) walls separated by a glass wall for compressive strength measurements at 1, 28 and 90 days. Sufficient mortar was made to fill on set of three 100 mm (3.9 in.) cubic steel molds for measurements of 1 day strength at 1 day curing in molds at 20°C (68°F).

EXPERIMENTAL RESULTS AND DISCUSSION

Rheology of paste

The flow curves of the pastes after 90 minutes are depicted in Fig. 1, while the Bingham viscosities and yield points as a function of time for the pastes are plotted in Fig. 2 and 3, respectively.

After 90 minutes from water addition, it can be seen from Fig. 1 that shear stresses at shear rates > 20 s⁻¹ is higher for paste with gypsum than pastes with other calcium

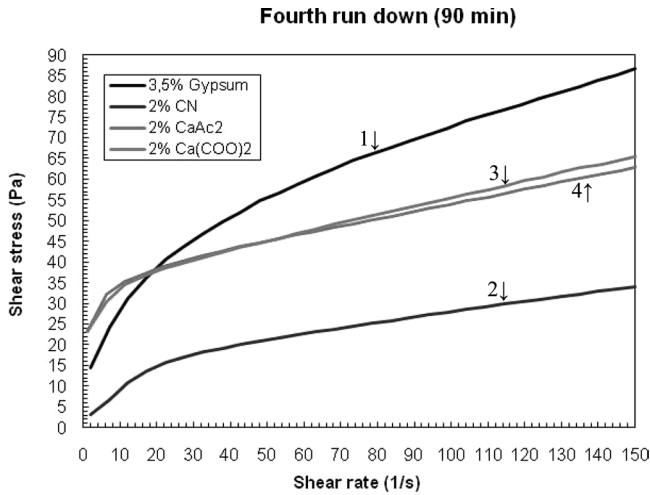


Fig. 1—Downward flow curves for clinker pastes made with 3.5% gypsum, 2% calcium nitrate, 2% calcium formate and 2% calcium acetate marked 1-4, respectively.

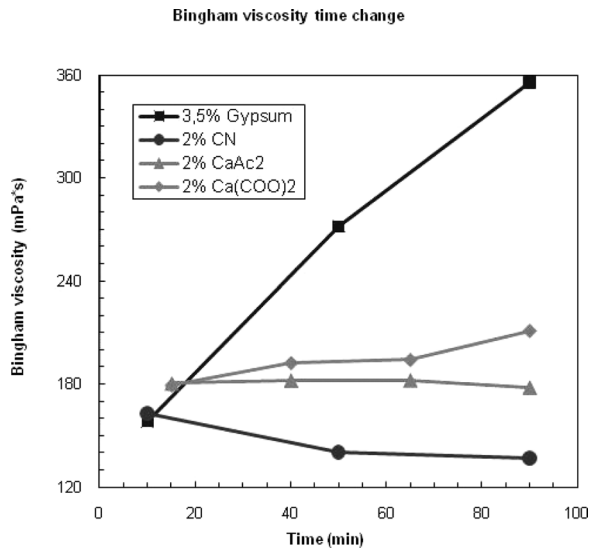


Fig. 2—Bingham viscosity as a function of time from water addition for clinker pastes made with 3.5% gypsum, 2% calcium nitrate (CN), 2% calcium formate, $\text{Ca}(\text{COO})_2$, and 2% calcium acetate, CaAc_2 .

salts replacing gypsum, and in particular much lower for the paste made with 2% calcium nitrate. The shear thinning effect is also more predominant for the paste with gypsum,

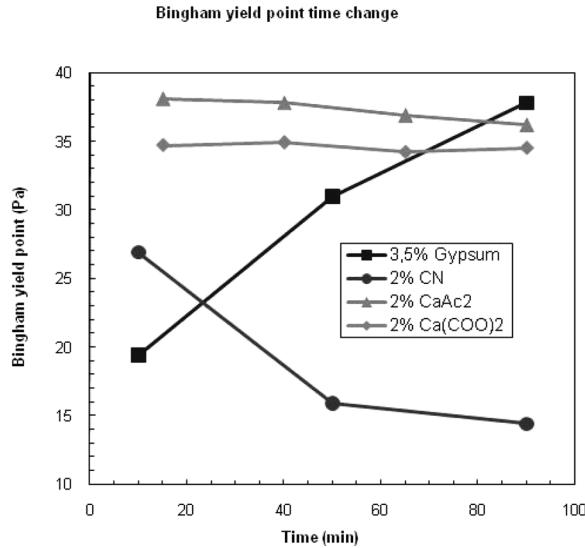


Fig. 3—Bingham yield point as function of time from water addition for clinker pastes made with 3.5% gypsum, 2% calcium nitrate (CN), 2% calcium formate, $\text{Ca}(\text{COO})_2$, and 2% calcium acetate, CaAc_2 .

perhaps because of the formation of needle shaped ettringite aligning in the direction of flow at higher shear rates. The other calcium salts are assumed to form more AFm type complexes (i.e. sulphate is replaced by two nitrate, acetate or formate anions) with C_3A having the form of platelets. Furthermore, ettringite transform 32 moles water from liquid to solid per mole C_3A reacted, whilst an AFm phase only transforms 11-12 moles water in comparison.

An increase in the volume fraction of solids (e.g. as a result of increased surface hydration) in a paste will lead to an increased resistance to flow as the apparent viscosity, $\eta \approx \tau / \dot{\gamma}$ (τ = shear stress and $\dot{\gamma}$ = shear rate), of fully dispersed slurries is a function of the volume fraction of solids, ϕ , according to the Krieger-Dougherty equation⁶

$$\frac{\eta}{\eta_c} = \left(1 - \frac{\phi}{\phi_m} \right)^{-[\eta]\phi_m} \tag{1}$$

where η_c is the apparent viscosity of the continuous phase (1 cP or 1 mPa·s [2.42 lb/ft·h] for water at 20°C), ϕ_m is the maximum volume concentration of solids (about 0.65) and $[\eta]$ is the intrinsic viscosity of the suspension given by

$$[\eta] = \lim_{\phi \rightarrow 0} \frac{\frac{\eta}{\eta_c} - 1}{\phi} \cong 5 \quad (2)$$

All independent variables; concentration, particle size distribution and particle shape, relate to the density at which particles are packed in suspension. Both ϕ_m and $[\eta]$ depend on shear stress, τ . For spherical particles ϕ_m is 0.63 at $\tau \rightarrow 0$ and 0.71 at $\tau \rightarrow \infty$. There is no theoretical basis of calculating ϕ_m for polydisperse particles, but it can be obtained empirically from viscosity of suspensions at various volume fractions.⁷

If one uses the values $\phi_m = 0.50$ and $[\eta] = 5.50$ as obtained for a series of cement slurries by Vikan and Justnes,⁸ the resulting volume fraction of solids $\phi = 0.4425$ for $w/c = 0.40$ and no hydration giving relative apparent viscosity 382 according to Eq. (1). If one makes the conservative assumptions of average specific density of 2.2 g/cm³ (0.079 lb/in.³) for early hydrates (Ettringite has specific density 1.78 g/cm³ [0.064 lb/in.³]) and 0.40 g (0.014 oz.) physical and chemical bound water per gram (0.035 oz.) reacted cement (probably higher in fresh state), a degree of hydration of only 2% will lead to a volume fraction of solids $\phi = 0.4560$ giving relative apparent viscosity 797 according to Eq. (1). This doubling in apparent viscosity serves as an illustration of the sensitivity of concentrated cement slurries to differences in surface hydration. The observed increase in apparent viscosity at 99 s⁻¹ from 10 to 90 minutes for the paste with 3.5% gypsum was from 354 to 731 mPa·s (0.238 to 0.491 lb/ft·s), while it actual decreased from 431 to 281 mPa·s (0.290 to 0.189 lb/ft·s) for the paste with 2% calcium nitrate (unknown reason, but may be due to changes in water binding over time).

To illustrate the character of early ettringite formation in fresh paste, a small amount of fresh OPC (7% C₃A and with gypsum) paste was dispersed in excess ethanol to stop hydration and a drop placed on a tape on a SEM specimen holder to dry out, carbon coated and investigated by SEM. The photo in Fig. 4 shows that long, thin ettringite needles form with length exceeding the size of individual cement grains. Even though this is taken from a cement paste from another unpublished study, it illustrates that such ettringite formation will lead to a higher volume fraction of solids as well as contributing to shear thinning effects for the flow curve. The implications of the rheology measurements are that cement can be made with lower water demand for equal flow, and perhaps with a lower slump loss due to the lack of continuous ettringite formation in the fresh state, if gypsum is replaced with other calcium salts.

Isothermal calorimetry of paste

The rate of heat evolution and cumulative heat of the clinker 1 pastes with the various calcium salts for the first 24 h are plotted in Fig. 5 and 6, respectively.

The rate of heat evolutions in Fig. 5 show that the characteristic double peak of AF_i to AF_m conversion at 6 to 12 h for paste with gypsum is absent for the pastes where gypsum is replaced with other calcium salts as set retarders (a smaller bump at later time when gypsum is replaced has unknown origin). This is as expected as very limited ettringite can form (i.e. only from sulphate in clinker) when gypsum is removed, and the questions arise whether or not such cements can be allowed to generate heat above 70°C (158°F)

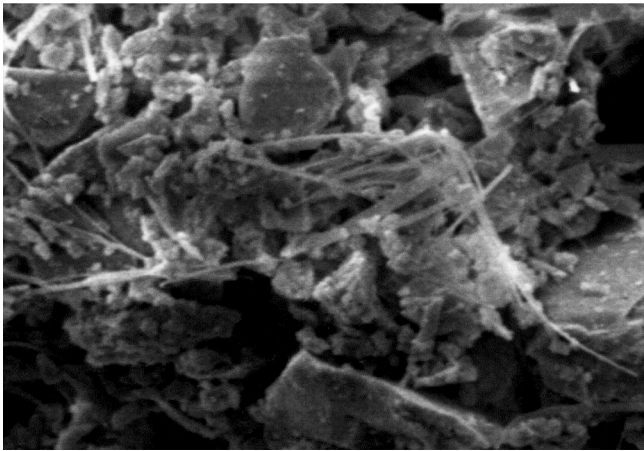


Fig. 4—SEM photo of dried fresh slurry of Portland cement allowed to hydrate for 30 minutes (unpublished experiment by Justnes).

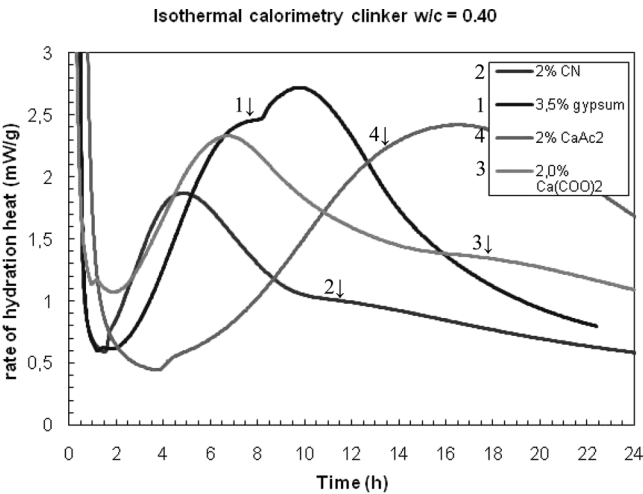


Fig. 5—Rate of heat evolutions first 24 h for clinker pastes made with 3.5% gypsum, 2% calcium nitrate, 2% calcium formate and 2% calcium acetate marked 1-4, respectively.

under semi-adiabatic conditions, or to be heat cured at higher temperatures (e.g. at pre-cast element plants), without the risk of detrimental delayed ettringite formation (DEF).

The rate of heat evolutions in Fig. 5 also indicates that pastes with 2% calcium formate and nitrate sets earlier than the paste with 3.5% gypsum indicating that these salts may retard C_3A at the same time as they actually accelerates the setting of C_3S . However, physical measurement of setting time by e.g. Vicat needle was not carried out. The 2% dosage

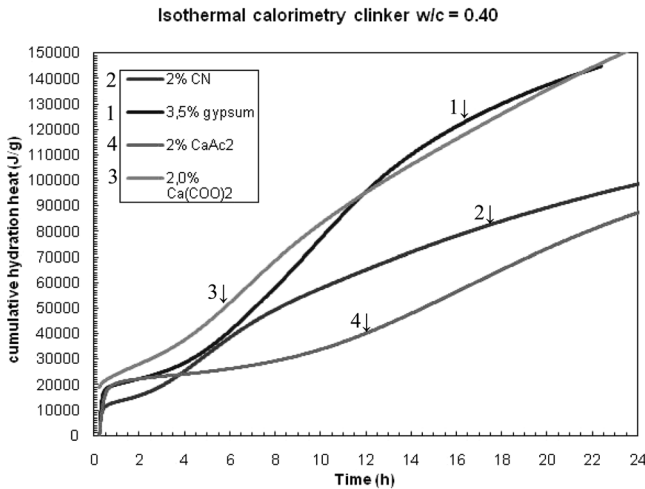


Fig. 6—Cumulative heat curves first 24 h for clinker pastes made with 3.5% gypsum, 2% calcium nitrate, 2% calcium formate and 2% calcium acetate marked 1-4, respectively.

of calcium acetate actually retards the setting, but smaller dosages will move the curve to shorter setting times (the author observed that 1.5% versus 2% calcium acetate parallel displaces the rate of hydration heat curve about 2 h to shorter times, but this is not reported here).

The cumulative heat of hydration curves plotted in Fig. 6 shows that paste with both 2% calcium nitrate and acetate evolves much less heat the first 24 h than paste with 3.5% gypsum and 2% calcium formate being about equal. This implies that it should be a possibility of making “low energy” cement for special applications (i.e. massive structures etc.) by simply replacing gypsum with calcium nitrate in the mill without altering the clinkering process at all! An alternative would of course be to make e.g. high-volume fly ash concrete for massive structures, but such large quantities of fly ash is not available everywhere and will pose a logistic challenge for the contractor. This “low energy” cement concept is checked out for mortar at semi-adiabatic conditions.

The rate of heat evolution and cumulative heat of the clinker 2 pastes with 3% gypsum, 2% calcium nitrate and without calcium salts for the first 24 h at 20°C (68°F) are plotted in Fig. 7 and 8, respectively. Clinker 1 had an immediate flash set when mixed with water without calcium salts so isothermal calorimetry was not measured, but clinker 2 had a few minutes open time so it could be placed in the glass vial of the calorimeter and be measured.

The first C_3A hydration peak of clinker 2 without admixture cannot be distinguished in Fig. 7, but the second C_3S peak is seen starting slowly at about 4 hours as this mineral has self-controlled setting. The rate of hydration heat for clinker 2 with gypsum is much steeper and is probably a combination of the initial hydration of C_3A and C_3S being accelerated by gypsum. The rate of hydration heat profile for clinker 2 paste with 2% calcium nitrate is starting about half an hour earlier than paste with gypsum since calcium nitrate accelerates set of C_3S but not hardening rate, and the maximum hydration rate is only half

Isothermal calorimetry clinker 2

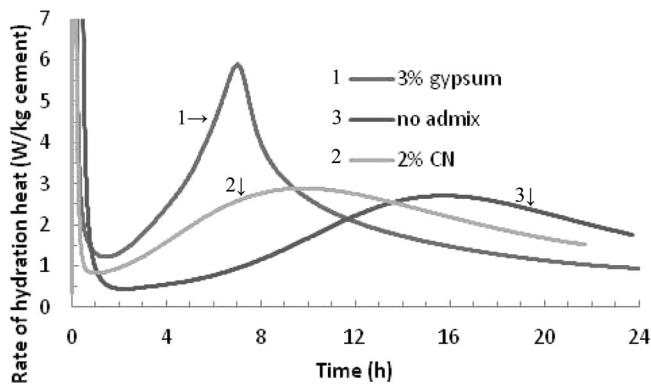


Fig. 7—Rate of hydration heat as a function of time at 20°C for clinker 2 paste ($w/c = 0.40$) with 3% gypsum, 2% calcium nitrate and no admixture marked 1-3, respectively.

Isothermal calorimetry clinker 2

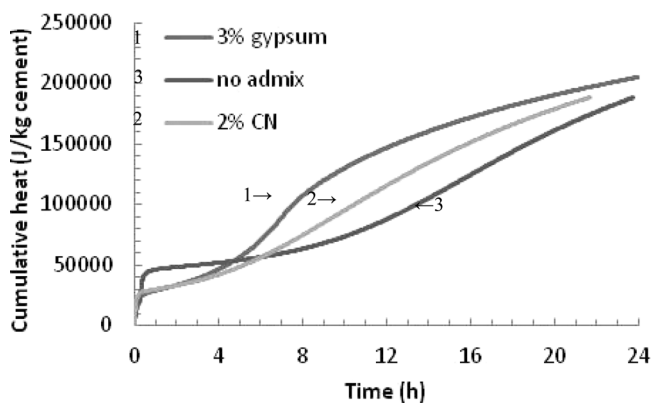


Fig. 8—Cumulative hydration heat as a function of time at 20°C for clinker 2 paste ($w/c = 0.40$) with 3% gypsum, 2% calcium nitrate and no admixture marked 1-3, respectively.

of the paste with gypsum due to lack of sulphate acceleration of C_3S and since calcium nitrate probably makes strong surface complexes with C_3A^9 (e.g. calcium nitrate is a strong retarder of high-alumina cement). The cumulative heat of hydration the first 24 hours show that it is nearly equal for the pastes with 3% gypsum and 2% calcium nitrate, which is reflected in about equal 1 day compressive strength (slightly higher for mortar with calcium nitrate) at 20°C (68°F) for mortar (see Table 3).

Table 3—Properties of mortars made with clinker 2

Mortar properties	w/ 3.5% gypsum	w/ 2% calcium nitrate
Fresh spread	162 mm (6.38 in.)	142 mm (5.59 in.)
1 day s_c 1 ℓ steel mould*	21.5 $\pm$ 0.2 MPa (3120 psi)	23.3 $\pm$ 0.4 MPa (3380 psi)
1 day mass 1 ℓ steel mould*	2305 $\pm$ 9 g (5.08 lb)	2318 $\pm$ 6 g (5.11 lb)
1 day s_c 1 ℓ styrofoam mould*	52.5 $\pm$ 0.7 MPa (7610 psi)	53.6 $\pm$ 0.0 MPa (7775 psi)
1 day mass 1 ℓ styrofoam mould*	2310 $\pm$ 3 g (5.09 lb)	2334 $\pm$ 6 g (5.15 lb)
28 day s_c 1 ℓ styrofoam mould†	59.6 $\pm$ 0.2 MPa (8,650 psi)	70.9 $\pm$ 0.4 MPa (10,300 psi)
28 day mass 1 ℓ styrofoam mould†	2345 $\pm$ 15 g (5.17 lb)	2362 $\pm$ 0 (5.21 lb)

*Average and standard deviation of three parallels.

†Average and standard deviation of two parallels.

Table 4—Expansion of heat-cured mortar after 9 months

Mix / Curing temperature	Length expansion, %
Mortar w/ 3.5% gypsum / 80°C (176°F) C	0.0219 $\pm$ 0.0011
Mortar w/ 3.5% gypsum / 20°C (68°F)	0.0103 $\pm$ 0.0003
Mortar w/ 2.0% calcium nitrate / 80°C (176°F)	0.0014 $\pm$ 0.0010
Mortar w/ 2.0% calcium nitrate / 20°C (68°F)	0.0109 $\pm$ 0.0003

Strength and expansion of heat-cured mortar

The change in DEF formation is being checked out by mortars with clinker 1 added 3.5% gypsum and 2% calcium nitrate, respectively, being heat cured at 80°C (176°F) for about 3 days after setting and being stored at 20°C (68°F) thereafter. Significant differences in expansion (see Table 4) have been observed (slightly more for 80°C (176°F) mortar with gypsum) after 9 months. As comparison, Meland et al.¹⁰ heat-cured concrete with w/c = 0.40 at 85, 70, and 20°C (185, 158, and 68°F), and it took about 4 months before significant differences in expansion was observed.

The flow and 1-day strengths of these mortars are given in Table 5. The result presented in Table 5 confirms the rheology measurement of paste in that the replacement of 3.5% gypsum with 2% calcium nitrate results in a higher flow (or lower flow resistance) at equal w/c . Furthermore, the much lower 1 day strength obtained at isothermal conditions after 1 day when 3.5% gypsum is replaced by 2% calcium nitrate confirms the lower cumulative heat of hydration observed by isothermal calorimetry. However, strength evolution of such cements will be higher under semi-adiabatic conditions even when significant lower maximum temperature is achieved simply by replacing gypsum with calcium nitrate.

Strength of mortar cured under semi-adiabatic conditions.

As seen from Table 3, the 1-day strength of clinker 2 mortar with 2% calcium nitrate was slightly higher than mortar with 3% gypsum, both cured at 20°C (68°F) in steel molds and semi-adiabatically in Styrofoam molds. The higher 1-day strength for mortar with 2% calcium nitrate cured in Styrofoam molds is achieved in spite of it reaching lower maximum temperature than mortar with 3% gypsum as seen in Fig. 9. However, at 28 days the compressive strength was about 71 MPa (10,300 psi) for mortar with 2% calcium nitrate as compared to about 60 MPa (8700 psi) for mortar with 3% gypsum as the same

Table 5—Spread of fresh mortar and 1-day compressive (σ_c) and flexural (σ_f) strength of mortar with 3.5% gypsum and 2% calcium nitrate as set retarders of Clinker 1

Property	3.5% gypsum	2% calcium nitrate
Spread 5 min	145 mm (5.71 in.)	170 mm (6.69 in.)
Spread 15 min	137 mm (5.39 in.)	166 mm (6.54 in.)
1 day σ_c	18.9 MPa (2740 psi)	7.1 MPa (1030 psi)
1 day σ_f	4.3 MPa (625 psi)	1.7 MPa (250 psi)

Note: s_c is compressive strength and σ_f is flexural strength.

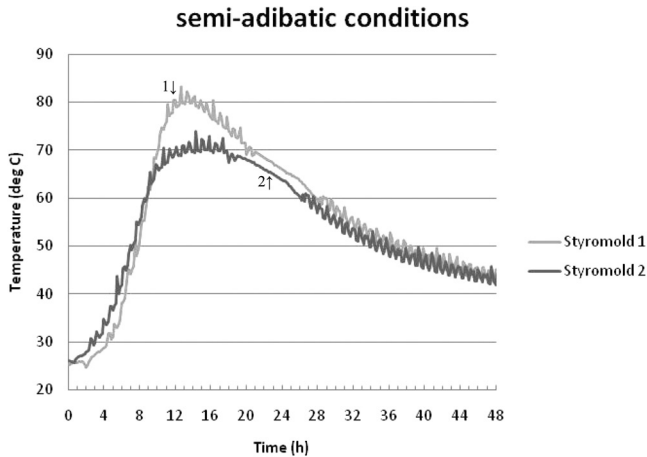


Fig. 9—Temperature evolution the first 48 h for clinker 2 mortar placed in 1 L Styrofoam molds with 3% gypsum and 2% calcium nitrate marked 1 and 2, respectively.

time as the difference in cube mass was less than 1% ruling out air content as explanation. The mass of the former was however always slightly heavier that could be explained by marginally better packing due to lack of gypsum that could have large impact on mature strength.

FURTHER RESEARCH

Further research will follow up the expansion of heat cured mortars in order to document any significant difference between gypsum and calcium nitrate in this matter. Finally, the microstructure of these mortars should be investigated. The concept of gypsum free cement should be documented for several other Portland cement clinkers in order to further document the effects observed in this paper.

CONCLUSIONS

Based on the results of this experimental investigation, the following conclusions are drawn:

1. Portland cement clinker can be set controlled by other calcium salts than gypsum, as demonstrated for calcium formate, acetate and nitrate.

2. The alternative calcium salts lead to a lower flow resistance of paste and mortar at equal w/c , and significantly less increase in flow resistance vs. time, than when gypsum is used.

3. A 2% calcium formate leads to about the same cumulative heat of hydration than for 3.5% gypsum the first 24 h, meaning that cement with similar strength development can be achieved. At the same time, such cement probably can be allowed to reach temperatures above 70°C (158°F) either in massive structures or by extensive heat curing in precast element factories without the risk of detrimental delayed ettringite formation (DEF).

4. A 2% calcium nitrate and acetate both leads to significant less cumulative heat evolution the first 24 h compared to 3.5% gypsum, while 2% calcium nitrate also leads to significant lower strength of mortar at 1 day when cured isothermally at 20°C (68°F) as expected from calorimetry. Semi-adiabatically cured mortar with 2% calcium nitrate gave 10°C (50°F) lower maximum temperature than mortar with 3% gypsum and 11 MPa (1600 psi) higher 28-day strength. This might imply that it could be possible to make “low energy” cement for special applications (i.e. massive structures etc.) by simply replacing gypsum with calcium nitrate in the mill without altering the clinkering process at all!

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A Novel Type of PCE Possessing Silyl Functionalities

by Julia Witt and Johann Plank

Synopsis: A series of silylated PCE polymers was prepared by aqueous free radical copolymerization using methacrylic acid, ω -methoxy poly(ethylene glycol) methacrylate ester and N-maleic γ -aminopropyl triethoxy silane (MAPS). The resulting copolymers possess silanol groups from alkaline hydrolysis of the triethoxy silane functionality in cement pore solution and thus can chemically interact with C-S-H phases. It was found that incorporation of MAPS significantly enhances the dispersing performance of ready mixed type PCEs possessing high grafting density while no improvement was observed for low grafted PCEs common in precast concrete. Adsorption tests revealed that MAPS increases adsorption of highly grafted PCEs, while adsorption of pre-cast type PCEs remains unaffected or even decreases.

Keywords: polycarboxylate, cement, silane, concrete

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INTRODUCTION

The invention of superplasticizers back in 1962 probably presents the most significant advance in concrete technology over the last 50 years. Application of these admixtures which are effective at surprisingly low dosages (as low as 0.02% by weight of cement) allows to produce a highly durable concrete, yet with excellent workability.¹ Due to their unique effects, we can now formulate self-compacting² and ultra-high strength concrete.³ These modern advanced concretes allow structures such as long-span bridges, high rise buildings etc. which were impossible before superplasticizers became known.

Nowadays, superplasticizers can be categorized into four chemically distinctly different classes: (1) polycondensates; (2) polycarboxylates; (3) “small molecules”; and (4) biopolymers.

Polycondensates represent the first type of superplasticizer invented in 1962. From this group, β -naphthalenesulfonate-formaldehyde (BNS) constitutes by far the most widely used type.⁴ Additionally, melamine-formaldehyde-sulfite (PMS),⁵ acetone-formaldehyde-sulfite (AFS)⁶ and sulfanilic acid-phenol-formaldehyde (SPF)⁷ polycondensates are utilized in specific applications. The advantages of polycondensate-type superplasticizers include relatively simple preparation from commonly available raw materials, robust performance with cements of variable compositions and high tolerance to contaminants occasionally occurring in cement such as e.g. clay and silt.

In 1981, polycarboxylate comb polymers were introduced as a new class of superplasticizers.⁸ Their structural characteristic is an anionic polymer backbone which holds lateral graft chains. These side chains instigate a steric hindrance effect between the cement particles suspended in water.⁹ Through this unique mechanism, PCE superplasticizers exhibit superior dispersing force compared to polycondensates. Because of their highly tunable chemical and molecular structure, PCEs can accommodate many different purposes such as providing long slump retention (2+ hours), effectiveness at ultra-low water-to-cement ratios ($w/c < 0.25$), or the so-called ‘Saratto–kan’ effect whereby concrete rapidly flows to its final spread (or slump) instead of creeping slowly. Consequently, a great diversity of chemically different PCE products is on the market which includes:

- **MPEG-type PCEs**, made from ω -methoxypoly(ethylene glycol) methacrylate ester (MPEG-MA), either by aqueous free radical copolymerisation¹⁰ or by esterification/transesterification reaction.¹¹
- **APEG-type PCEs**, made from α -allyl- ω -methoxy or hydroxy poly(ethylene glycol) (APEG) ether and maleic anhydride as key monomers via radical copolymerization

either in bulk or in aqueous solution.¹² Comonomers such as styrene are frequently used as so-called spacer molecules to adjust the conformational flexibility of the trunk chain. This method provides polymers with pronounced stiffness or more coiled conformation and hence modifies their adsorption behavior.

- **VPEG-type PCEs**, based on vinyl ethers such as 4-hydroxy butyl-poly(ethylene glycol) vinyl ether which is co-polymerized at low temperatures ($< 30\text{ }^{\circ}\text{C}$) with e.g. maleic anhydride.¹³
- **IPEG-type PCEs** (in China also referred to as TPEG-type PCE) made from isoprenyl oxy poly(ethylene glycol) macromonomers by copolymerization with acrylic acid, for example.¹⁴ Recently, this type of PCE has become very popular because of its easy preparation from versatile raw materials.
- **HPEG-type PCEs** utilize methallyl- ω -methoxy or hydroxy poly(ethylene glycol) ether as macromonomer.¹⁵ Note: In some company literatures, the term HPEG-type PCE is applied to **MPEG-type PCEs** where the poly(ethylene glycol) side chain is hydroxy terminated instead of methoxy.
- **XPEG-type PCEs** represent slightly cross-linked PCEs; they are made from monomers which possess two reactive double bonds (e.g. diethylene glycols or diesters) and this can provide some degree of crosslinking.¹⁶
- **PAAM-type PCEs**: these zwitter-ionic PCEs possess polyamidoamine (PAAM) side chains; this structural feature distinguishes them fundamentally from all other PCEs which contain PEO/PPO side chains. The PAAM-type PCE is said to fluidify cement at w/c ratios as low as 0.12.¹⁷

The chemical structures of the types of PCEs described above are displayed in Fig. 1.

In addition to PCEs, 'small molecule' based superplasticizers are utilized to some extent as well. The most prominent example contains a diphosphonate as anchoring group which is linked to a poly(ethylene glycol) side chain.¹⁸ Finally, casein (a milk protein) is also utilized as superplasticizer in dry-mix mortar formulations such as self-leveling compounds (SLCs).¹⁹ It provides a honey-like consistency to cement pastes which is highly desirable in SLCs. Such flow characteristic is however less desirable in concrete.

In spite of the huge arsenal of currently available superplasticizers, the industry still tries to further improve this technology, with a clear focus on PCEs. Currently, the main thrust is to present novel PCE structures which are more robust with diverse cement compositions, which are not subject to desorption by free dissolved sulfate (the so-called 'sulfate effect') and can tolerate contaminants such as clays. One recent example of such novel structures are hyperbranched PCEs.²⁰

In this study, novel PCEs possessing silyl functionalities were synthesized and their dispersion effectiveness and working mechanism was investigated. For this purpose, MPEG-type PCEs containing silyl functionalities were prepared by free radical copolymerization from methacrylic acid, MPEG-methacrylate ester and N-maleic acid- γ -amidopropyl triethoxy silane (MAPS) at different molar ratios. The polymers were characterized with respect to their elemental composition, molar masses and anionic charge amount. Dispersion effectiveness of the silylated PCEs was probed via 'mini slump' test on cement pastes. To clarify the working mechanism, adsorption of these polymers on cement was quantified.

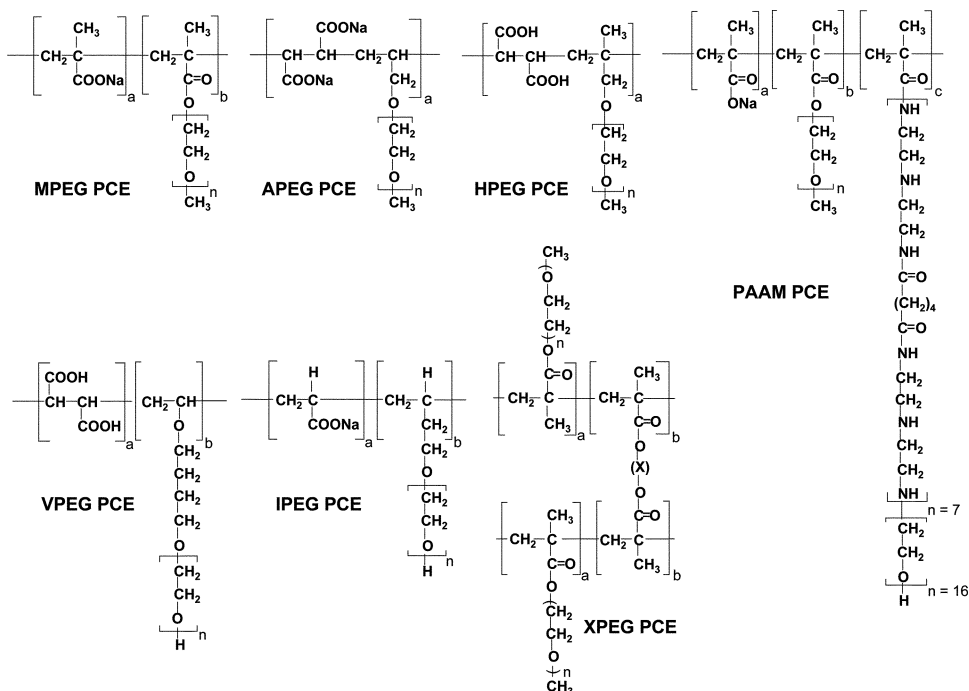


Fig. 1—Chemical structures of PCE type superplasticizers currently applied by the concrete industry.

RESEARCH SIGNIFICANCE

The motivation behind the study of silylated PCEs was to clarify whether such PCEs can interact with the surfaces of the silicates present in cement. It is known that anionic superplasticizers adsorb almost exclusively on aluminate hydrates such as ettringite or mono-sulfoaluminate. It was hoped that the silanol groups formed after alkaline hydrolysis of the siloxane functionality can undergo a condensation reaction with $\equiv\text{Si}-\text{OH}$ groups present on the surfaces of hydrating $\text{C}_3\text{S}/\text{C}_2\text{S}$. The aim was to attain a PCE which is not only physically sorbed, but chemically bound to cement through a covalent bond. Such PCE would be completely robust against desorption e.g. from sulfate, and thus exhibit extremely stable performance.

EXPERIMENTAL PROCEDURES

Synthesis of silyl monomer

γ -amidopropyl triethoxy silane (APS, obtained from Wacker Chemie AG, Burghausen/Germany) was reacted in situ with maleic anhydride (VWR International, Darmstadt/Germany) following an $\text{S}_\text{N}2$ mechanism to yield the N-maleic γ -amidopropyl triethoxy silane (MAPS) monomer, as is shown in Fig. 2. Under the conditions selected here, maleic anhydride reacts with one carboxylate functionality only to the mono amide, because the cyclic anhydride is much more reactive than the ring-opened maleic acid. For preparation,

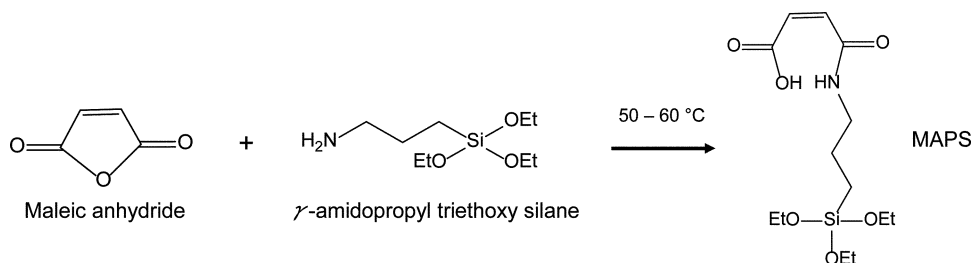


Fig. 2—Synthesis of *N*-maleic γ -amidopropyl triethoxysilane (MAPS) monomer.

a 500 mL three-neck round bottom flask is charged with 221 g (1.23 mol, a slight excess) of APS and stirred at 200 rpm. To this liquid, 98 g (1.00 mol) of maleic anhydride are added in small portions over a total period of 1 hour. Immediately, an exothermic reaction between APS and maleic anhydride occurs, and the temperature has to be kept at $50 - 60\text{ }^{\circ}\text{C}$ by using a cold water bath. Following the addition of maleic anhydride, the viscous mixture is stirred for another 15 minutes to complete the reaction before it is cooled to ambient. The reaction product is a white, waxy solid which exhibits a sharp melting point at $38\text{ }^{\circ}\text{C}$. ^1H NMR analysis confirmed its composition to be $\sim 87\text{ wt. \%}$ MAPS and $\sim 13\text{ wt. \%}$ unreacted, excess APS.

Preparation of PCE polymers

Seven polymers were synthesized according to the reaction scheme shown in Fig. 3. Five of them contained silyl functionalities while the remaining two were unmodified reference polymers. The raw materials and quantities used in each preparation are shown in Table 1. In a typical synthesis, a 500 mL five-neck round bottom flask is charged with 90 mL of DI water, stirred at 200 rpm and purged with nitrogen for 20 minutes. Thereafter, the required quantity of methacrylic acid is added and neutralized with equimolar amount of solid NaOH. After all NaOH has dissolved, MAPS is introduced and again is neutralized with stoichiometric amount of NaOH. Then, the chain transfer agent sodium methallylsulfonate (Aldrich, Munich/Germany) and the monomer MPEG methacrylate ester ($n_{\text{EO}} = 45$; 50% aq. solution from Aldrich, Munich/Germany) are charged into the flask. The mixture is adjusted to a pH of 9.2 using a 30 wt. % aqueous NaOH and heated to $60\text{ }^{\circ}\text{C}$. During the addition of all raw materials, nitrogen purging is continued and a total of 187.5 mL of DI water is used in small portions to rinse the containers holding the monomers and thus ensuring complete transfer into the reaction flask. At $60\text{ }^{\circ}\text{C}$, 15 mL of an aqueous solution containing 2.5 g of $\text{Na}_2\text{S}_2\text{O}_8$ initiator are added over a total period of 30 minutes by using a peristaltic pump (MCP standard, Ismatec Laboratoriumstechnik GmbH, Wertheim-Mondfeld/Germany; addition rate is 0.167 mL of initiator solution per minute). After completion of initiator dosing, stirring continues for 30 minutes at $60\text{ }^{\circ}\text{C}$ and another hour at $80\text{ }^{\circ}\text{C}$ before the liquids are cooled to ambient. The PCE solutions are yellowish or brownish viscous solutions with solids contents between 17 and 29 wt. %.