SP-288.01

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 μeq/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

***Lei Lei** is a Master student at the School of Materials Science, University of Zhengzhou, China. In 2011, she participated in an exchange program with Technische Universität München and researched on novel types of superplasticizers.*

***Johanna de Reese** studied chemistry and currently works on her Ph.D. thesis at the Chair for Construction Chemicals, TU München. Her focus is on the thermodynamics of superplasticizer adsorption on cement and the interaction of superplasticizers with solid particles in general.*

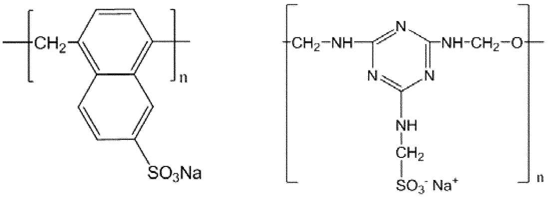
***Johann Plank** is full Professor at the Institute of Inorganic Chemistry of Technische Universität München, Germany. Since 2001, he holds the Chair for Construction Chemicals there. Research interests include cement chemistry, chemical admixtures, organic-inorganic composite and nano materials, concrete, dry-mix mortars and oil well cementing.*

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-compacting[2] or ultra-high strength concrete[3] were made possible only through the use of these highly advanced superplasticizers.

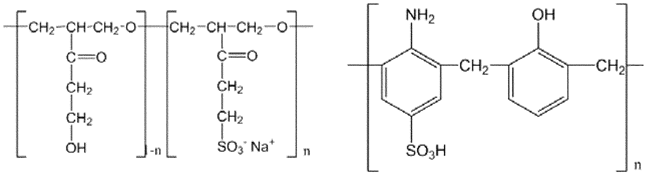
Generally, superplasticizers can be categorized into four chemically distinctly different groups: (1) polycondensates; (2) polycarboxylates; (3) "small molecules"; and (4) biopolymers. Polycondensates were the first type of superplasticizer invented in 1962 independently by Aignesberger from SKW Trostberg, 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



β-naphthalene sulfonate formaldehyde (BNS)

Melamine formaldehyde sulfite (PMS)



Acetone formaldehyde sulfite (AFS)

Sulfanilic acid phenol formaldehyde (SPF)

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_3S, monoclinic	66.7
C_2S, monoclinic	15.0
C_3A, cubic	4.9
C_3A, orthorhombic	3.5
C_4AF, orthorhombic	2.3
$CaSO_4$	1.9
$CaSO_4 \cdot 1/2H_2O$[*]	0.5
$CaSO_4 \cdot 2H_2O$[*]	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 (d_{50} value, determined by laser granulometry) was found at 11.08 µm and its *Blaine* fineness was 3 424 cm^2/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, d_{50} value 12.75 µm, Blaine fineness 3610 cm^2/g; CEM II B-V 42.5 R (Spenner, Erwitte, Germany) 72.5% clinker, 2.5% anhydrite and 25% coal fly ash, d_{50} value 10.81 µm, Blaine fineness 3947 cm^2/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, d_{50} value 8.89 µm, Blaine fineness 4 322 cm^2/g.

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

Oxide	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	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 cm^2/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 $Na_2S_2O_5$ (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. % Na_2SO_4.

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 $CaSO_4 \cdot 2H_2O$, 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.

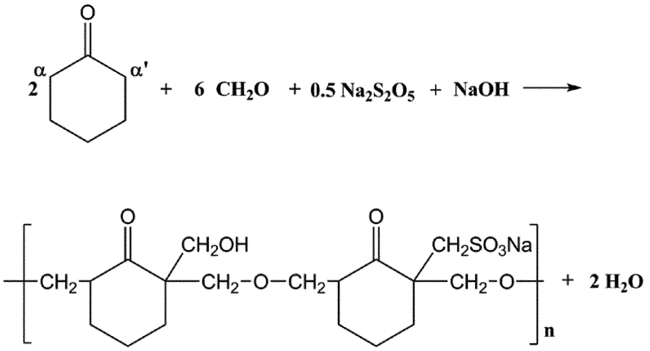


Fig. 2—Synthesis route and molecular structure of novel CFS superplasticizer.

EXPERIMENTAL RESULTS AND DISCUSSION

Synthesis and characterization of CFS

The novel CFS superplasticizer was synthesized from cyclohexanone, formaldehyde and sodium pyrosulfite at a molecular ration of 1:3:0.25 using an aldol condensation process. There, under strongly alkaline conditions (pH ≥ 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 $Na_2S_2O_5$. 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.

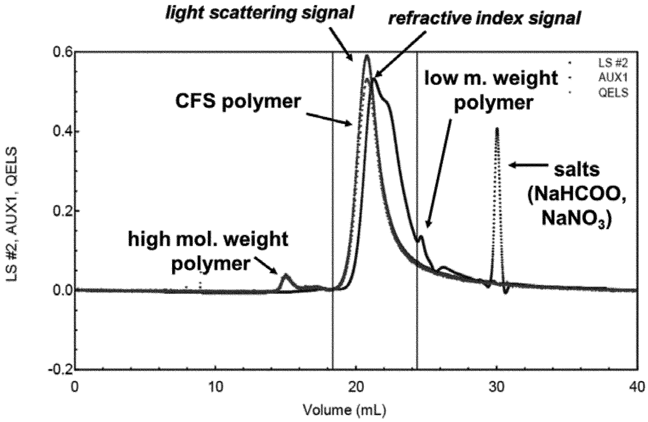


Fig. 3—Size exclusion chromatogram of CFS purified by dialysis.

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, µeq/g			
	Synthesized CFS	Purified CFS	BNS	PCE
DI water	1340	2980	4090	1055
Synthetic cement. pore solution	1100	2680	3910	351

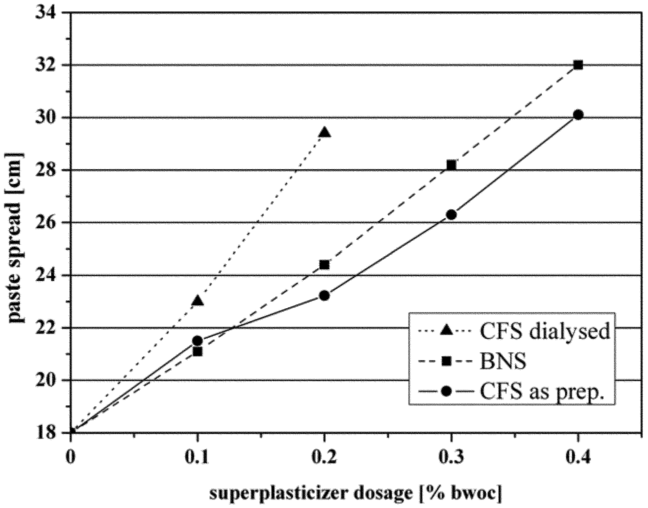


Fig. 4—Spread flow of cement pastes (w/c = *0.55) containing different dosages of CFS as prepared, of purified CFS and of commercial BNS sample. (Note: 1 mm = 0.039 in.).*

"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