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Synthesis, working mechanism and effectiveness of a novel cycloaliphatic superplasticizer for concrete[☆]

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ABSTRACT

In this study, the synthesis, performance and mode of action of a new type of superplasticizer is presented. From cyclohexanone, formaldehyde and sulfite, a high molecular weight polycondensate ($M_w \approx 220{,}000$ g/mol) was synthesized. The resulting CFS superplasticizer was characterized by size exclusion chromatography and anionic charge density measurement. Performance of CFS in cement was probed by mini slump test and by determining the maximum water reduction achievable. The working mechanism was identified via adsorption and zeta potential measurements. The results show that CFS behaves like a typical polycondensate superplasticizer such as BNS. It enhances the fluidity of cement due to electrostatic repulsion. Advantages of this novel type of superplasticizer are simple preparation method, effectiveness at low water-to-cement ratio, huge water reducing capability and stable performance in the presence of clay.

1. Introduction

Nowadays, the use of superplasticizers in concrete is very common [1–3]. Superplasticizers improve fluidity of concrete by dispersing cement particles present in the paste. High-performance concrete that includes high-fluidity concrete and high-strength concrete only can be produced with advanced superplasticizers [4].

In 1959, superplasticizers were first applied in oil well cementing in Oklahoma [5]. After that, for concrete, in 1962 SKW company in Germany discovered poly(melamine sulfonate) (PMS), and in the same year Kao Soap in Japan invented poly(naphthalene sulfonate) (BNS) superplasticizer [6]. The advent of these two polycondensate based superplasticizers indicates the beginning of a new era in concrete technology. With the aid of this new type of admixture, it suddenly was possible to produce very durable concrete possessing low water-to-cement ratio and at the same time excellent workability. From the 1970s, these two polycondensates were extensively used and experience was gained in their application [7,8]. Also, their working mechanism and their interaction with cement hydrates were clarified [9–13].

Experience in the application demonstrated that BNS is an effective superplasticizer for standard conditions. It does not work well, however, at low water-to-cement ratios (<0.35). Additionally, its fluidizing effect rapidly diminishes after addition to concrete (short slump retention) [14]. For PMS, a similar trend was found. It does however not introduce any air into concrete and therefore is ideal for precast concrete, whereas BNS, because of a slightly longer slump retention, became the preferred admixture in ready mix concrete applications, particularly in combination with sodium gluconate retarder.

Because of these shortcomings of BNS and PMS, in 1981 an aliphatic superplasticizer based on acetone formaldehyde sulfite (AFS) polycondensate was developed as a new type of high range water-reducing agent [15,16]. Compared to BNS and PMS, its advantages are inexpensive raw materials, simple synthetic process and effectiveness at low water-to-cement ratios [17]. Because of its high temperature stability, salt tolerance and a synergistic effect with cellulose ethers, it has become the predominant dispersant in oil well cementing [18]. In concrete applications, however, its intensive red color is a big disadvantage.

In China, another polycondensate type superplasticizer based on sulfanilic acid, phenol and formaldehyde (SPF) was invented [19]. Its properties are mostly comparable to that of AFS, the differences being the much less intensive color of SPF and a better slump loss behavior stemming from a minor retarding effect of the phenolate functionality. As a result, SPF has become quite popular in China and is more widely used there than PMS or AFS.

Because all polycondensates are quite tolerant to different cement compositions and are relatively inexpensive, they are still widely used. Globally, the main types are poly(naphthalene sulfonate) and poly(melamine sulfonate).

However, their poor slump retention characteristics remained a problem. As a result, in the 1980s, polycarboxylate superplasticizers were introduced as a new generation of concrete admixtures [20]. They are effective at lower dosages than polycondensates, and specific molecular structures provide excellent slump retention [21,22].

[☆] This article is dedicated to Dr. Aignesberger and Dr. Hattori, the two pioneers of polycondensate superplasticizers, on occasion of their 85th birthday.

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Recently, it has become obvious that PCEs are quite sensitive to different cement compositions (e.g. because of the sulfate effect) and that they interact strongly with clay which can occur as an impurity in aggregates and limestone. Additionally, they cause excessive foaming which needs to be controlled by the addition of defoamers. Because of these shortcomings of PCEs, polycondensate-based superplasticizers have experienced renewed attention only recently.

From the above, it is obvious that the different kinds of superplasticizers possess specific advantages, but also drawbacks. Therefore, new chemical structures for advanced superplasticizers need to be probed. Here, we report on a novel cycloaliphatic superplasticizer which has been synthesized from cyclohexanone, formaldehyde and sulfite (CFS). Its effectiveness in cement with respect to flow improvement and water reduction capability and its principle working mechanism were studied. Additionally, its dispersing performance in the presence of clay was probed. The overall goal was to obtain an idea whether CFS represents an admixture which is more tolerant to clay than the superplasticizers known so far.

2. Experimental

2.1. Materials

Cyclohexanone (99% purity), formaldehyde (30 wt.% aqueous solution), sodium sulfite (>96.0% purity), formic acid (100% purity) and solid sodium hydroxide all were purchased from VWR International (Darmstadt, Germany) and used as is.

Melcret®500F superplasticizer supplied by BASF SE, Ludwigshafen, Germany was used for comparison. It is a purified and spray dried powder of BNS polycondensate and possesses low Na_2SO_4 content (<2 wt.%).

In the clay contaminated cement paste, a polycarboxylate superplasticizer named 45PC6 synthesized in our laboratory was used for comparison. Its molar masses, polydispersity index and hydrodynamic radius are presented in Table 1. This PCE was prepared by aqueous radical copolymerization of methacrylic acid and ω-methoxy poly (ethylene oxide) methacrylate ester using methallyl sulfonic acid as a chain transfer agent. The molar ratios of the monomers were 6:1:0.2, and the number of ethylene oxide units in the side chain was 45. The synthesis process is described in detail in [23].

The cement used in this study was an ordinary portland cement (CEM I 42.5 R Milke®classic from HeidelbergCement, Geseke plant). Its phase composition as determined by QXRD using *Rietveld* refinement is presented in Table 2. The average particle size (d_{50} value, determined by laser granulometry) was found at 12.02 μm and its density at 3.16 g/cm^3 (Helium pycnometer).

As clay, a commercially available Na^+-montmorillonite named RXM 6020 manufactured by Rockwood (Moosburg, Germany) was used. This clay is a naturally occurring Na-bentonite, and was used as per obtained. The major components of the clay as determined by XRF are shown in Table 3.

2.2. Synthesis of CFS

In a 2-L round-bottomed flask equipped with a reflux condenser and a thermometer, at room temperature 32 g (0.25 mol) of sodium sulfite was dissolved under vigorous stirring in 150 mL of 30 wt.% aqueous formaldehyde solution. The pH value of the solution was adjusted to ~13.5 by addition of 13.3 mL of 30 wt.% aqueous NaOH solution. The solution warms to approximately 35 °C and is cooled back to room temperature. As soon as sodium sulfite is dissolved completely, 50 g of cyclohexanone is added quickly. After about 1 min, the emulsion will turn into a clear solution, become yellow and turbid and start to boil vigorously. After boiling, the solution becomes clear again, at the same time the color changes from yellow to brownish and the viscosity increases. The solution is heated to reflux for about 3 h under constant stirring using an oil bath (120 °C). Then, the aqueous CFS solution (~50 wt.% concentration) is cooled to room temperature and the pH value is adjusted to 10.3 by addition of formic acid. Some physical properties of the CFS solution, such as solid content, pH, color and viscosity are shown in Table 4.

Table 1
Molar masses, polydispersity index (PDI) and hydrodynamic radius (R_h) of synthesized CFS, purified CFS, PCE sample 45PC6 and of the commercial BNS sample.

Polymer	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)	$R_{h(z)}$ (nm)
Synthesized CFS	218,800	96,550	2.3	7.9
Purified CFS	342,200	97,820	3.5	9.5
BNS	139,100[a]	–	–	–
PCE	163,100	45,570	3.6	10.2

[a] Batch measurement.

Table 2
Phase composition of CEM I 42.5 R determined by QXRD using Rietveld refinement.

Phase	wt.%
C_3S, m	70.1
C_2S, m	11.0
C_3A, c	5.1
C_3A, o	2.1
C_4AF, o	2.5
Free lime (Franke)	0.9
Periclase (MgO)	0.0
$CaSO_4$	2.5
$CaSO_4 \cdot 0.5H_2O$[a]	0.3
$CaSO_4 \cdot 2H_2O$[a]	0.4
Calcite	3.3
Quartz	0.7

[a] Measured by thermogravimetry.

2.3. Characterization of CFS

Here, molar masses, polydispersity index (PDI) and hydrodynamic radius (R_h) of CFS were determined by size exclusion chromatography (SEC). Additionally, the anionic charge density was measured.

2.3.1. Size exclusion chromatography (SEC)

A CFS solution containing 10 g/L of the polymer was prepared for SEC analysis. Measurement was performed 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, USA). 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. CFS concentration in the eluent was 10 mg/mL. From the SEC measurements, the polydispersity index (PDI), the molar masses (M_w and M_n) as well as the hydrodynamic radius (R_h) were obtained. The value of dn/dc used to calculate M_w and M_n was 0.135 mL/g (value for polyethylene oxide) [24].

2.3.2. Specific anionic charge density

The specific anionic charge densities of the polymers were determined by a particle charge detector PCD 03 pH (Mütek Analytic,

Table 3
Oxide composition (wt.%) of RXM 6020 clay as determined by XRF.

Oxide	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	TiO_2	LOI[a]	Total
(wt.%)	59.73	18.39	0.79	2.25	3.96	2.32	0.13	0.11	12.3	99.96

[a] LOI = loss of ignition, measured at 1000 °C.

Table 4
Physical properties of the synthesized CFS solution.

Property	Value
Solid content [wt.%]	49.52
pH	10.3
Color	Brownish red
Viscosity [mPa.s][a]	864

[a] Measured on a Brookfield viscometer (Model HA, equipped with # 3 spindle).

Herrsching, Germany). This method allows the experimental determination of the anionic charge of polymers in solution. Here, 0.2 g/L of the polymers was 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 was 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.

2.4. Performance test in cement

The performance of CFS in cement was tested by measuring paste flow, slump loss over time and the maximum water reduction achievable.

2.4.1. Mini slump test

For the determination of the paste flow, a “mini slump test” according to DIN EN 1015 was utilized and carried out as follows:First, the water-to-cement (w/c) ratio of the paste without polymer was set to give a spread of 18 ± 0.5 cm. At this w/c ratio, the dosages of polymers required to reach a spread of 26 ± 0.5 cm 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 1 min to the mixing water, then rested for 1 min without stirring and were again stirred for 2 min manually 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) 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.

2.4.2. Time dependent slump loss behavior

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 stirred again for 2 min. Measurements were taken every 15 min and total period of the measurement was 120 min.

2.4.3. Maximum water reduction achievable with CFS

First, w/c ratio of the paste without polymer was set to produce a spread of 26 ± 0.5 cm. Next, dosages of CFS in steps of 0.3% by weight of cement (bwoc) were added and the w/c ratio at which the paste exhibits a spread of 26 ± 0.5 cm 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.

2.5. Investigation of the working mechanism

For this purpose, adsorption of CFS onto cement particles, and the zeta potential in cement paste were determined.

2.5.1. Adsorption measurement

Superplasticizer adsorption on cement was measured using the depletion method. The non-adsorbed portion of polymer remaining in solution at equilibrium condition was determined by analyzing the total organic content (TOC) of the solution. In a typical experiment, 16 g of cement, 8 g of DI water and the amount of superplastizer to be tested were filled into a 50 mL centrifuge tube and shaken in a wobbler (VWR International, Darmstadt, Germany) for 2 min at 2400 rpm and then centrifuged for 10 min at 8500 rpm. The supernatant was diluted with deionized water. 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 1 h of stirring with values obtained after 2 min of stirring only. In both cases, the same values were obtained.

2.5.2. Zeta potential

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.

The zeta potentials of freshly prepared cement pastes (w/c ratio = 0.5) containing 0–1.0% bwoc of CFS and BNS, respectively, were measured under continuous stirring.

3. Results and discussion

First, the dispersing power of the new polycondensate superplasticizer was probed in comparison to BNS using different test methods. This was followed by an investigation of its working mechanism using adsorption and zeta potential results.

3.1. Synthesis and characterization of CFS

The novel CFS superplasticizer was synthesized from cyclohexanone, formaldehyde and sodium sulfite using an aldol condensation process. There, under strongly alkaline conditions, cyclohexanone reacts with formaldehyde in α position to the ketone functionality by forming methylol groups. Subsequently, sulfite reacts 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. 1. Using this synthesis method, a yellowish or brownish, slightly viscous liquid with ~50 wt.% solid content is achieved.

The synthesized polycondensate was characterized using SEC. From there, the molar masses (M_w, M_n), the polydispersity index (PDI) and the hydrodynamic radius (R_h) of the solved macromolecule were determined. Additionally, the same properties were obtained for a CFS sample purified by dialysis, and for the commercial BNS superplasticizer sample. The results are shown in Table 1.

The data signify that the synthesized CFS still contains some impurities (oligomers. by-products and residual starting materials), as became evident from the SEC diagrams (not shown here). This effect is highlighted by the increased molecular weight of purified CFS which stems from the removal of low molecular and oligomeric by-products.

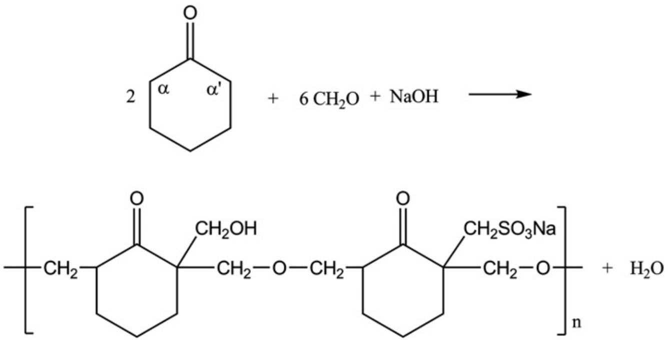

Fig. 1. Synthesis route and molecular structure of CFS superplasticizer.

Compared with BNS, the CFS sample prepared here exhibits a much longer main chain.

Next, the anionic charge densities of synthesized and purified CFS and of BNS were determined in DI water and synthetic cement pore solution, respectively. The results are exhibited in Table 5. 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 Ca^{2+} ions present in cement pore solution, it shields some of the negative charge of the polyelectrolytes. According to the data shown in Table 5, CFS possesses a lower anionic charge density than BNS. This was also confirmed by zeta potential measurements presented in Section 3.4.2.

3.2. Cement dispersion effectiveness

The dispersion force of CFS was determined by using two different methods: (1) the increase in paste flow as a function of CFS dosage and (2) the water reduction achievable at different CFS dosages.

3.2.1. Mini slump test of cement paste

In this test, a cement paste prepared at a w/c ratio of 0.5 which exhibited a spread of 18 ± 0.5 cm was used as reference. As is shown in Fig. 2, CFS as prepared dispersed cement very well. At dosages exceeding 0.7%, increased bleeding of the paste occurred. This effect is expressed by the higher fluctuation of the spread values at these dosages.

As expected, purified CFS exhibited higher dispersion force than the CFS sample obtained in the synthesis. The performance of purified CFS is comparable to that of the commercial BNS sample which in the manufacturing process also underwent a purification step to remove excessive Na_2SO_4. Thus, it is demonstrated that the active polymer part contained in CFS is as effective as purified BNS polymer.

3.2.2. Water reduction achievable with CFS

In this test, a cement paste prepared at a w/c ratio of 0.63 which exhibited a spread of 26 ± 0.5 cm was used as a starting system. Subsequently, pastes containing dosages of 0.1–1.2% bwoc of CFS at incremental steps of 0.1% were prepared. 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. 3. There, it becomes obvious that CFS possesses a high water reduction capability. For example, at a dosage of 0.3% bwoc which is typical for actual application of polycondensates, the water reduction achieved was 21%. The maximum water reduction found with CFS was 52% at 1.2% bwoc dosage. This value compares well with that achievable from polycarboxylates [25]. It confirms the exceptional dispersion force of new CFS superplasticizer.

Table 5
Specific anionic charge density of superplasticizer samples tested.

Fluid system	Specific anionic charge density [μeq/g]		
	Synthesized CFS	Purified CFS	BNS
DI water	2037	2598	4089
Synthetic cement pore solution	1951	2167	3911

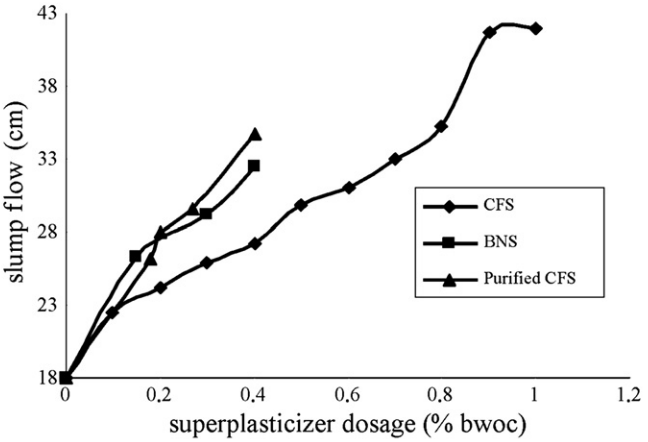

Fig. 2. Spread flow of cement pastes (w/c = 0.5) containing different dosages of CFS as prepared, of purified CFS and of commercial BNS superplasticizer.

According to Fig. 3, the CSF for lowest w/c ratio attainable with this cement was 0.30. Comparative testing revealed that BNS worked to a w/c ratio of 0.32 (BNS dosage required there: 1.0% bwoc) while the PCE sample performed till a w/c ratio of 0.25 (dosage 0.8% bwoc). This data signifies that CFS is susperior over common polycondensate superplasticizers, but is inferior to specific PCE products which sometimes work at w/c values as low as 0.20.

3.2.3. Time dependent slump loss behavior

The slump loss of a cement paste prepared at a w/c ratio of 0.5 and a CFS dosage of 0.3% bwoc corresponding to a paste flow of 26 ± 0.5 cm was determined over a period of 2 h. According to Fig. 4, the slump of this cement paste quickly decreased in the first 40 min, while it decreased slower afterwards. Such behavior is typical for polycondensate type superplasticizers.

3.2.4. Impact on cement hydration kinetics

To detect a potential retarding effect of CFS, time-dependent heat evolvement from a cement paste (w/c ratio = 0.5) holding 0.27% bwoc of CFS, BNS and polycarboxylate sample 45PC6 was monitored. The results are exhibited in Fig. 5. There, it is demonstrated that, similar to BNS, CFS does not much influence the hydration kinetics of OPC. Particularly, no retardation was observed. This behavior explains the rapid decrease of slump flow over time observed for the cement

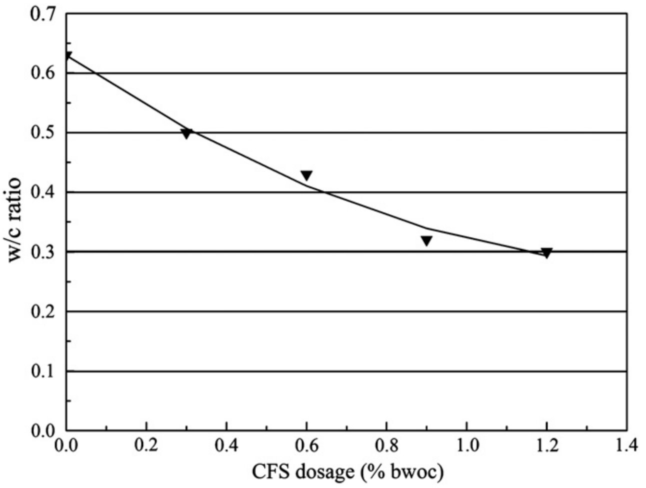

Fig. 3. Water reduction capability of synthesized CFS as a function of dosage.

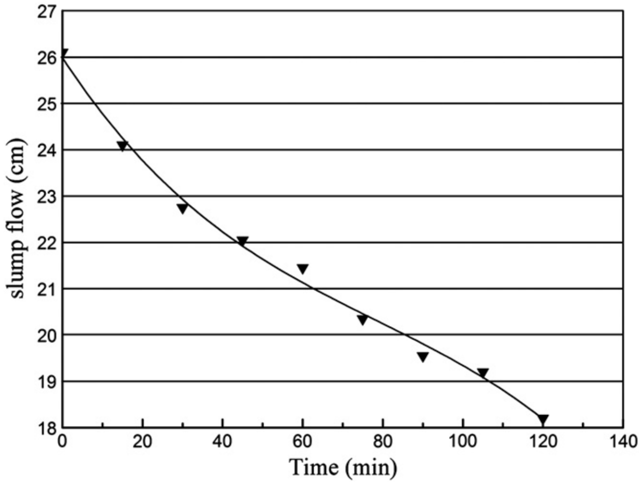

Fig. 4. Slump loss behavior of a cement slurry (w/c = 0.5) containing 0.3% bwoc of CFS as prepared.

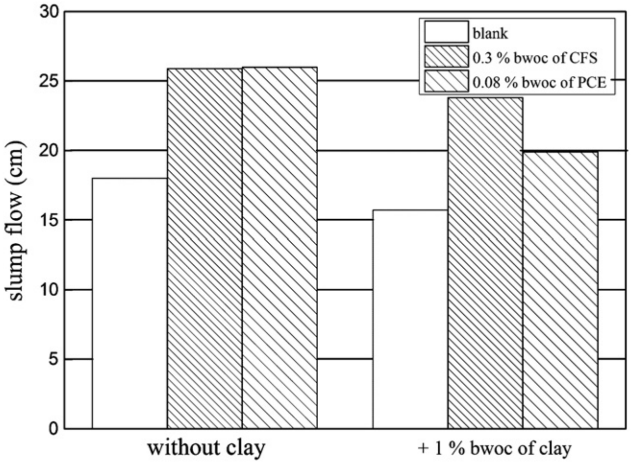

Fig. 6. Spread flow of cement pastes (w/c = 0.5) containing 0.3% bwoc of CFS or 0.08% bwoc of PCE, measured in absence and presence of 1% bwoc of clay.

slurry containing CFS. Contrary to this, the PCE sample noticeably delayed cement hydration. Such behavior is characteristic for most polycarboxylate superplasticizers.

3.3. Behavior of CFS in presence of clay

In this test, cement pastes prepared at a w/c ratio of 0.5 which exhibited a spread of 18 ± 0.5 cm were used. 0.3% bwoc of CFS and 0.08% bwoc of PCE both gave a spread of 26 ± 0.5 cm when added to this slurry. As is shown in Fig. 6, 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

3.4. Working mechanism of CFS

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

3.4.1. Adsorption on cement

In this test, the w/c ratio of the cement paste was set to 0.5. Fig. 7 shows that CFS strongly adsorbed on cement, as a result of its highly anionic character. The adsorption isotherm for CFS on cement is of *Langmuir* type. At low dosages, the adsorbed amount of CFS increased quickly and then gradually approached a constant value of ~4 mg/g of cement, which represents the point of saturation adsorption. This signifies that complete coverage of the surface of cement particles was achieved at a CFS concentration of 1.2% bwoc. This result corresponds very well with the findings on the water reduction capability displayed in Fig. 3. There, maximum water reduction was achieved at the same dosage of 1.2% bwoc.

The results allow to conclude that CFS achieves cement dispersion by adsorption on the cement surface, thus instigating a highly negative charge. Accordingly, the working mechanism of CFS is based on electrostatic repulsion of cement particles.

3.4.2. 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. 8.

In this test, aqueous CFS solution was titrated to a cement paste possessing a w/c ratio of 0.5. The zeta potential of the paste was measured at increasing CFS dosages of up to 1% bwoc. As shown in Fig. 8,

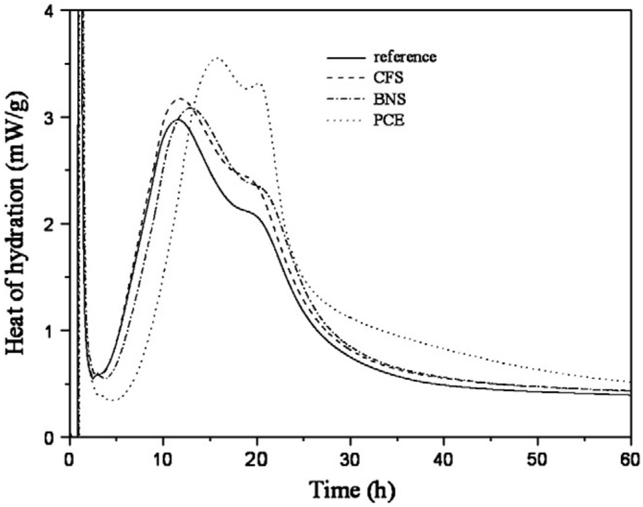

Fig. 5. Time-dependent heat evolvement from cement paste (w/c = 0.5) holding 0.27% bwoc of synthesized CFS, BNS and PCE superplasticizer respectively.

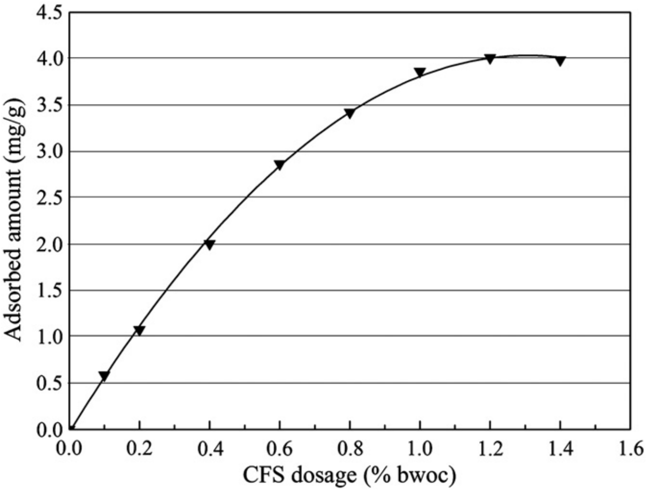

Fig. 7. Adsorption isotherm for CFS superplasticizer on cement (CEM I 42.5 R).

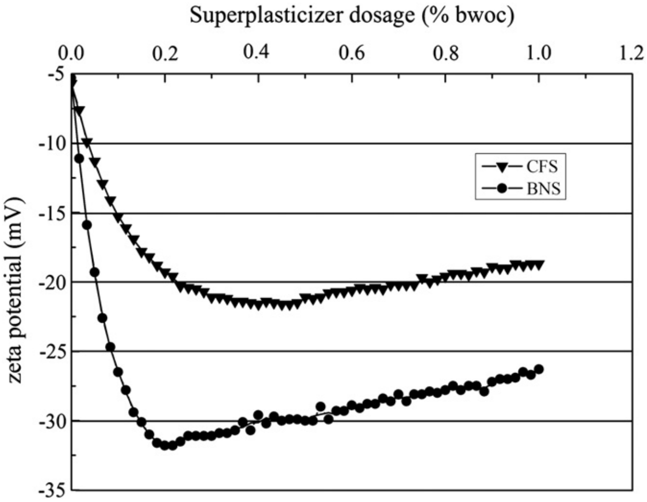

Fig. 8. Zeta potential of cement slurry (w/c = 0.5) as a function of superplasticizer dosage.

at CFS dosages lower than 0.4% bwoc, the zeta potential which was −5.7 mV for the cement paste without CFS rapidly decreased to ~ −22 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, the electrostatic repulsion mechanism 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 [26,27].

4. Conclusions

A CFS polycondensate was synthesized from cyclohexanone, formaldehyde and sulfite. The results show that CFS behaves like a typical polycondensate superplasticizer such as BNS. It enhances the fluidity of cement paste due to electrostatic repulsion. The sulfonate groups present in CFS are negatively charged. They undergo physisorption on the positively charged mineral surfaces of cement hydrates, thus giving them a negative charge, which creates electrostatic repulsion and overcomes attractive forces between the cement particles. This results in the disintegration of cement agglomerates into primary particles and a significant decrease in the viscosity of the pastes. This way, a highly workable cement paste without segregation or bleeding is achieved.

The results confirm that the novel cycloaliphatic superplasticizer can be prepared as a ~50 wt.% solution using a simple method, exhibits a high water reduction capability which is ~50%, is effective at low w/c ratios (up to 0.30) and shows robust performance even in the presence of clay. Compared with BNS it offers the advantages of casein synthesis which, for example, does not require porcelain lined pressurized reactors. Over AFS, another popular ketone–aldehyde polycondensate, CFS is superior because cyclohexanone possesses a much lower flammability and volatility than acetone and therefore is much easier to handle on industrial scale. Additionally, the problem of the intense dark-red color of AFS which is highly disadvantageous in handling and applying this material does not occur with CFS which possesses a very light color only.

Another aspect of CFS is its stability with respect to release of free formaldehyde. The aqueous CFS solution as prepared showed a free CH_2O content of < 0.01 wt.% which did not change after 3 months storage. In contrast, melamine based superplasticizers are known to gradually release formaldehyde because of their rather instable amino methylol groups. This poses a potential problem during handling and application of PMS superplasticizers and requires addition of a CH_2O scavenger. Finally, CFS exceeds PCE type superplasticizers with regard to higher tolerance for cement and concrete contaminants, namely clay. This way, CFS enlarges the arsenal of currently available superplasticizers.

Acknowledgments

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