Modification of the Molar Anionic Charge Density of Acetone–Formaldehyde–Sulfite Dispersant to Improve Adsorption Behavior and Effectiveness in the Presence of CaAMPS®-*co*-NNDMA Cement Fluid Loss Polymer

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ABSTRACT: Sulfonated aldol polycondensates were synthesized from acetone, formaldehyde, and different amounts of sodium sulfite, resulting in polymers with varying degrees of sulfonation (DS). The anionic charge amount of these macromolecules measured by polyelectrolyte titration decreased with lower DS. The effectiveness of the acetone–formaldehyde–sulfite (AFS) polycondensates as cement dispersant was found to depend on the amount of polymer adsorbed on cement. AFS adsorption decreases with lower DS. Interaction and compatibility between AFS and CaAMPS®-*co*-NNDMA fluid loss additive was studied by formulating binary additive systems composed of one of the modified AFS polymers and CaAMPS-*co*-NNDMA. At high DS, AFS adsorbs strongly and prevents CaAMPS-*co*-NNDMA from adsorbing in sufficient amounts on the cement surface. The result is poor fluid loss control of the cement slurry. AFS polymers with lower DS, however, allow simultaneous adsorption of both polymers in sufficient quantities to provide good fluid loss control and low rheology at the same time. Thus, effectiveness of both additives was retained. Obviously, effectiveness of such multi-admixture systems depends on the adjustment of the adsorption behavior of the individual components relative to each other. Molar anionic charge density of the polymers was found to be a major parameter influencing their relative adsorption behavior. The AFS polymer with DS = 0.2 possesses a molar anionic charge density comparable to CaAMPS-*co*-NNDMA. Thus, when admixtures with similar molar anionic charge densities are used, the performance of one component is not negatively influenced by the other. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2018–2024, 2009

Key words: water-soluble polymers; adsorption; AMPS®; polycondensation; oil well cement

INTRODUCTION

In oil well cementing, water-soluble polymers are applied to adjust the properties of cement pastes.[1] Dispersants ensure the pumpability of the cement suspension over a distance of several kilometers. Fluid loss additives (FLAs) reduce uncontrolled water loss from the slurry pumped along the porous formation of the bore hole.[2–4]

Sulfonated naphthalene formaldehyde and sulfonated melamine formaldehyde polycondensates are two typical superplasticizers used commercially in construction applications.[5] In oil well cementing, acetone–formaldehyde–sulfite (AFS) polycondensate is preferred because of its superior effectiveness in salt slurries.[6] Adsorption of these anionic additives on the positive surface areas of hydrating cement creates negatively charged particles. The resulting electrostatic repulsion between the cement grains leads to disagglomeration of the solids.[5] It decreases the viscosity of cement pastes and reduces the pressure required to pump the slurry through the annulus of the borehole.

Former studies revealed an adsorptive working mechanism for AFS dispersant and for poly(*N*,*N*-dimethylacrylamide-*co*-Ca 2-acrylamido-2-methylpropanesulfonate) (CaAMPS®-*co*-NNDMA) FLA.[7] In a binary admixture system, these two additives compete for the limited number of adsorption sites on the cement surface. As a consequence of this competitive adsorption, CaAMPS-*co*-NNDMA is displaced from the cement surface by stronger adsorbing AFS. Thus, fluid loss control of the cement slurry declines with increasing AFS dosage. Such unwanted effects severely impact the technical performance and economics of the admixture combination. This example perfectly illustrates the general problems associated with multicomponent admixture systems which are frequently used in oilfields, construction, paper, textile, and other applications. A very recent study showed that in the presence of AFS, the adsorption behavior of CaAMPS-*co*-NNDMA is strongly

TABLE I
Phase Composition (XRD, Rietveld), Specific Density, Specific Surface Area (Blaine), and d_{50} Value of API Class G Oil Well Cement Sample

C³S (wt %)	59.6
C_2S (wt %)	22.8
C_3A_c (wt %)	1.2
C_4AF (wt %)	13
Free CaO (wt %)	<0.3
$CaSO_4 \cdot 2H_2O$ (wt %)	2.7[a]
$CaSO_4 \cdot {}^1/_2 H_2O$ (wt %)	0.0[a]
$CaSO_4$ (wt %)	0.7
Specific density (kg/L)	3.18
Specific surface area (m^2/kg)	305.8
d_{50} value (µm)	9.8

C_3S: tricalcium silicate ($Ca_3(SiO_4)O$); C_2S: dicalcium silicate (Ca_2SiO_4); C_3A_c: cubic modification of tricalcium aluminate ($Ca_9Al_6O_{18}$); C_4AF: tetra calcium aluminate ferrite ($Ca_4Al_2Fe_2O_{10}$).
[a] Measured by thermogravimetry.

influenced by the type and molar amount of anchor groups.[8] For example, incorporation of only 1–2 mol % of maleic anhydride produces a polymer which adsorbs in equally high amounts in the presence and absence of AFS. Thus, fluid loss of the cement slurry remains unchanged when AFS is added. A disadvantage of this approach is that in other frequently applied admixture combinations, CaAMPS-*co*-NNDMA must not adsorb as strongly to allow other additives to function. Furthermore, the modification of the chemical structure of AFS to improve the compatibility appears to be comparatively easier than modification of FLA.

Thus, the aim of this investigation was to modify the sulfonated acetone–formaldehyde superplasti-cizer with respect to its adsorption behavior and to achieve a sufficient amount of adsorption of both FLA and AFS. For this purpose, several AFS polymers with different degrees of sulfonation (DS) were synthesized. Their specific anionic charge densities were determined by charge titration. Fluid loss control and rheology of cement slurries containing the modified AFS dispersants and unmodified CaAMPS-*co*-NNDMA were measured and the adsorption of both additives was determined.

EXPERIMENTAL

Materials

Oil well cement

An API Class G cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) according to American Petroleum Institute (API) Spec. 10A was used. Phase composition, specific density, particle size (d_{50} value), and specific surface area of the sample are presented in Table I.

AFS polycondensates

An aldol-type reaction was used to synthesize the AFS polycondensates. Figure 1 describes their formation and proposes a chemical structure for the resulting polycondensate. Despite the long history of such aldol reactions, their different steps are still unknown.[9,10] The analysis of samples taken during early stages of our reaction confirmed the presence of high amounts of diacetone alcohol and formaldehyde–sulfite adduct. The chemical structure proposed in Figure 1 is based on IR and ^{1}H NMR data.
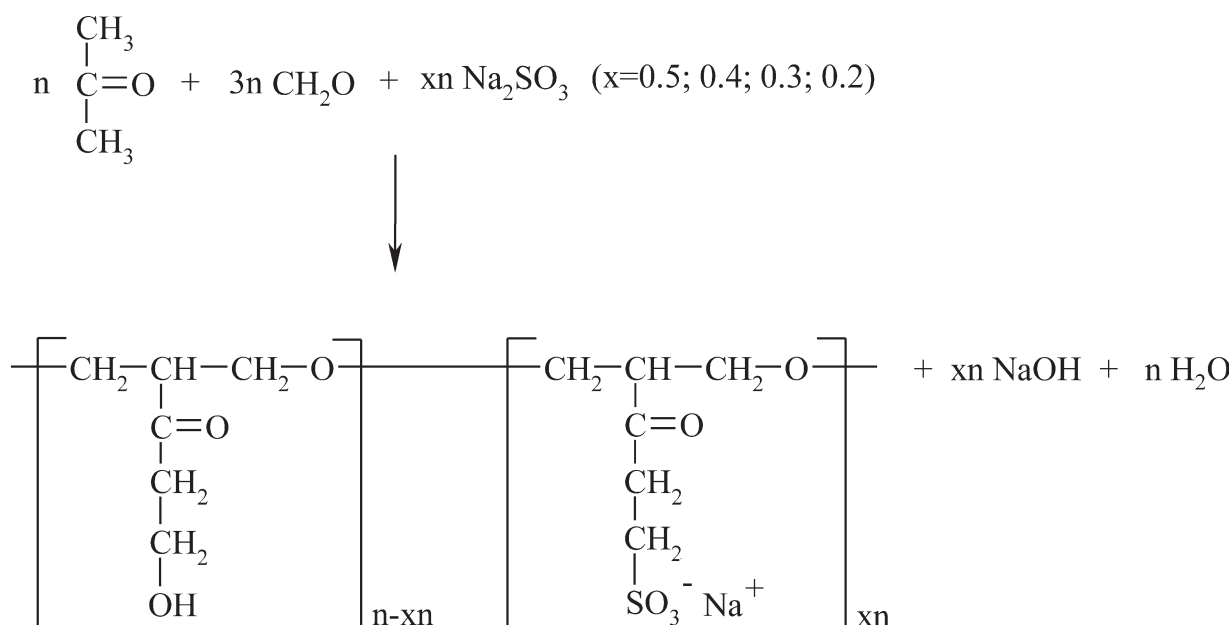
Figure 1 Synthesis of acetone–formaldehyde–sulfite (AFS) polycondensate.

For the synthesis of the AFS samples, a modified version of the procedure described by Aignesberger and Plank was used.[6,11] In a 1-L three-necked, round-bottomed flask equipped with a reflux condenser and a thermometer, sodium sulfite was dissolved in DI water at 50°C by vigorous stirring. After cooling to 40°C, acetone (58.08 g, 1 mol) was added. The reaction flask was then kept at 40°C for 1 h with constant stirring. Because of the highly exothermic character of the aldol reaction, aqueous formaldehyde of 30% concentration (300.0 g, 3 mol) was gradually fed into the reactor through a dropping funnel. The first 10th of the solution was added dropwise over a period of 30 min and then stopped, while the increasing temperature was maintained at 60–65°C by cooling with cold water. Formaldehyde addition was continued once the reaction mixture had turned red and the acetone reflux had faded away. Temperature was allowed to rise to 90–95°C and the reaction continued for 2 h. Three samples of AFS with different molar amounts of sodium sulfite (0.4, 0.3, and 0.2 mol per mol of acetone) were synthesized, characterized, and compared with a reference AFS sample synthesized from 0.5 mol Na_2SO_3 and used in previous studies.[7,8]

AMPS®-co-NNDMA fluid loss polymer

The copolymer of N,N-dimethylacrylamide (NNDMA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was synthesized by aqueous free radical polymerization as previously reported.[7,8] The liquid polymer was drum dried at 150°C, yielding a white powder. AMPS was obtained from Merck-Schuchardt (Darmstadt, Germany). NNDMA was obtained from Sigma-Aldrich Chemical (Munich, Germany). The chemical structure of CaAMPS-co-NNDMA is presented in Figure 2.

Poly(DADMAC)

A 0.001N solution of poly(diallyl-dimethyl-ammoniumchloride) obtained from BTG Mytek GmbH (Herrsching, Germany) was used as cationic polyelectrolyte.

Instruments

Gel permeation chromatography

A Waters Alliance 2695 (Waters, Eschborn, Germany) equipped with RI detector 2414 (Waters, Eschborn, Germany) and a dynamic light scattering detector (Dawn EOS; Wyatt Technologies, Clinton, IA) was used. AFS separation was performed by using Ultrahydrogel 500, 250, and 120 columns (Waters) and a 3-angle dynamic light scattering detector, whereas FLA was separated on a precolumn and two Aquagel-OH 60 columns (Polymer Labora-
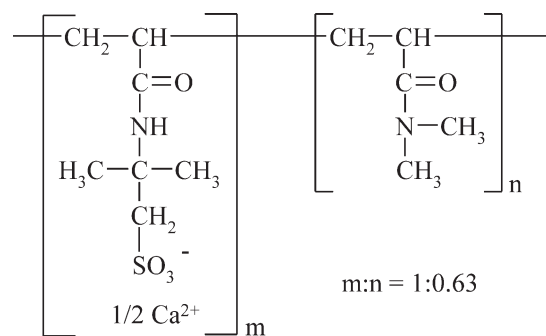
Figure 2 Chemical structure of CaAMPS®-co-NNDMA copolymer.

tories, distributed by Varian, Darmstadt, Germany). For FLA, an 18-angle dynamic light scattering detector was used.

Charge titration

PCD 03 pH (Mütek Analytic, Herrsching, Germany) and a blue ribbon filter paper obtained from Whatman® (Dassel, Germany) were used.

Cement testing

Phase composition of the cement sample was determined using an XRD instrument (D8 Advance; Bruker AXS, Karlsruhe, Germany) with Bragg-Bretano geometry. The diffractometer is equipped with a scintillation detector using Cu Kα ($\lambda = 1.5406$ Å) radiation with a scanning range between 5° and 80° 2θ at a scanning speed of 0.5 s/step (with 0.008°/step). Specific density of the cement was measured on an Ultrapycnometer® 1000 (Quantachrome Instruments, Boynton Beach, FL). The average particle size (d_{50}) measurement was carried out using a laser-based particle size analyzer (Cilas 1064, Marseille, France). The specific surface area was determined with a Blaine instrument (Toni Technik, Berlin, Germany). A blade-type laboratory blender manufactured by Waring (Torrington, CT) was used. The slurry was homogenized in the atmospheric consistometer (model 1250; Chandler Engineering, Tulsa, OK).

API filtration cell

A 500-mL OFITE high-temperature high-pressure filter press (part no. 171-00-C; OFI Testing Equipment, Houston, TX) was used.

Rheology

A Couette-type coaxial cylinder rotational viscometer, FANN 35SA (Fann Instruments Company, Houston, TX) equipped with R1 rotor sleeve (rotor radius:

1.84 cm), B1 bob (bob radius: 1.7245 cm, bob height: 3.8 cm), and F1 torsion spring was used.

Adsorption

High TOC II (Elementar, Hanau, Germany) with CO_2 and NO detector was used.

Procedures

GPC separation

AFS: The molecular weights (M_w, M_n) of the synthesized AFS samples were determined by GPC. Aqueous $0.1M$ $NaNO_3$ (adjusted with NaOH to pH 12) was used as an eluant at a flow rate of 1.0 mL/min. The AFS solutions were filtered through a 0.2-μm filter and measured. A dn/dc of 0.177 mL/g (value for poly(sodium 4-styrene sulfonate)) was applied. Thus, all measured molecular weights are relative to poly(sodium 4-styrene sulfonate).[12]

CaAMPS-*co*-NNDMA: M_w and M_n of the copolymer were determined using a $0.2M$ $NaNO_3$ aqueous solution (adjusted with NaOH to pH = 9) as an eluant at a flow rate of 1.0 mL/min. FLA solution was filtered through a 5-μm filter. The value of dn/dc used to calculate M_w and M_n was 0.156 mL/g (value for polyacrylamides).[13] Thus, the molecular weights measured are relative to polyacrylamide.

Cement slurry preparation

Cement slurries were prepared in accordance with the test procedure set forth in Recommended Practice for Testing Well Cements, API Recommended Practice 10 B, issued by the American Petroleum Institute, using API Class G oil well cement and deionized water.[14] The cement slurry was mixed at a water-to-cement ratio of 0.44 using the Waring blender. First, 700 g cement and 3.5 g (0.5% by weight of cement, bwoc) CaAMPS-*co*-NNDMA powder were dry blended. Next, 1.4 g (0.2% bwoc) AFS were dissolved in 308 g water and transferred into the 1500-mL cup of the Waring blender. Then, the cement/CaAMPS-*co*-NNDMA blend was added

within 15 s to the aqueous AFS solution and mixed for 35 s at 12,000 rpm. To ensure homogeneous consistency, all slurries were poured into the 500-mL slurry container of an atmospheric consistometer and stirred for 20 min at 27°C.

API static fluid loss

Static fluid loss was determined at 27°C following API RP 10B procedure using a 500-mL HTHP filter press.[14,15] After pouring the homogenized cement slurry into the filter cell, a differential pressure of 70 bar (N_2) was applied at the top of the cell. Filtration proceeded through a 3.5-in.[2] mesh metal sieve placed at the bottom of the cell. The filtrate produced by the differential pressure was collected for 30 min (V_{30}). As described by API RP 10B, the collected filtrate volume was doubled and designated as API fluid loss of the corresponding cement slurry.

Rheology

Rheology of the cement slurry was determined following API RP 10B procedure using the FANN 35SA rotational viscometer.[14] The homogenized cement slurry obtained after stirring in the atmospheric consistometer was poured into the 300-mL cup of the FANN rheometer. Shear stress (lbs/100 ft^2) was measured at shear rates of 600, 300, 200, 100, 6, and 3 rpm. The initial instrument dial reading was taken 1 min after continuous rotation at 300 rpm. The following readings were taken in ascending order after continuous rotation for 20 s at each speed. Finally, the reading at 600 rpm was taken.

Charge titration

The specific anionic charge amounts of AFS and FLA, respectively, were determined in cement pore solution by charge titration using poly(diallyl-dimethyl-ammoniumchloride) as cationic polyelectrolyte. Cement pore solution was prepared by vacuum filtration of the cement slurry without additives using a blue ribbon filter paper. Charge titration was

TABLE II
Properties of Sulfonated Acetone-Formaldehyde Dispersant Samples and FLA

Type of polymer	Molar ratio of acetone : formaldehyde : sulfite	Molecular weight		Polydispersity index M_w/M_n	Radius of gyration Rg$_z$ (nm)	Specific anionic charge amount ε of polymer[a] (C/g)
		M_w (g/mol)	M_n (g/mol)			
AFS	1 : 3 : 0.5	64,000	16,000	4.0	9.0	243
AFS	1 : 3 : 0.4	63,000	11,000	5.5	14.0	210
AFS	1 : 3 : 0.3	62,000	12,000	5.4	13.9	178
AFS	1 : 3 : 0.2	47,000	12,000	3.9	17.7	112
FLA	–	1,800,000	1,200,000	1.5	85.2	337

[a] Measured in cement pore solution.

TABLE III
Calculation of Molar Anionic Charge Amount and Molar Anionic Charge Density of Sulfonated
Acetone-Formaldehyde Dispersant Samples and FLA

Type of polymer	Molar ratio of acetone : formaldehyde : sulfite	Molar anionic charge amount ε_m (C/mol)	Radius of the molecule R (nm)	Volume of the molecule V (nm^3)	Molar anionic charge density Θ [C/(mol nm^3)]
AFS	1 : 3 : 0.5	1.6×10^7	12	7.2×10^3	2222
AFS	1 : 3 : 0.4	1.3×10^7	18	2.4×10^4	542
AFS	1 : 3 : 0.3	1.1×10^7	18	2.4×10^4	458
AFS	1 : 3 : 0.2	5.3×10^6	23	5.1×10^4	104
FLA	–	6.1×10^8	110	5.6×10^6	109

performed with a solution prepared from 9 mL cement pore solution and 1 mL of a 0.2 g/L solution of either AFS or FLA.

Adsorption

The amount of admixture adsorbed on cement was determined from the filtrate collected in the fluid loss test. Achievement of adsorption equilibrium was checked by comparing polymer adsorption in cement slurry stirred for 20 min in the atmospheric consistometer with a slurry which was not stirred. In both cases, the same values for adsorbed amount of polymers were found. The adsorbed amount was calculated from the difference in the equilibrium concentrations of the polymers in the liquid phase before and after adsorption. When only AFS was present in the cement filtrate, its concentration was measured by TOC analysis. When both admixtures were present, FLA concentration was determined by TN analysis. The adsorbed amount of AFS was determined by subtracting the adsorbed amount of FLA determined by TN analysis from the sum of adsorbed amounts of FLA and AFS measured by TOC analysis. For TN analysis, the alkaline cement filtrate containing the unadsorbed polymers obtained from the fluid loss test was adjusted to neutral pH by adding 0.01M phosphoric acid.

RESULTS AND DICUSSION

Effect of DS

Table II lists the characteristic properties of the synthesized AFS samples. The decrease of DS does not

significantly affect the molecular weight of the polymers. The polydispersity indices which were found to lie between 3.9 and 5.5 indicate a kinetically controlled polycondensation.[16] Furthermore, it was found that the specific anionic charge amount ε of the polymers depends on the molar amount of sodium sulfite used in the synthesis. It decreases steadily when less sulfonate groups are incorporated into AFS (see Table II).

A critical parameter determining the adsorbed amount of a polymer is the molar anionic charge density.[17] In our study, the procedure of Lechner et al. was used to calculate these values for each polymer.[18] Assuming that the polymers are hard spheres, their molecular radius can be obtained from $R = (5/3 \ Rg_z^2)^{0.5}$, where Rg_z is the experimentally determined radius of gyration (see Table II). In the next step, the volume of the molecules can be calculated according to $V = 4/3 \cdot \pi \cdot R^3$. Further, the molar anionic charge amount $\varepsilon_m = \varepsilon \cdot M_w$ is derived from the experimentally measured values of the specific anionic charge amount ε and the weight average molecular weight M_w of the polymers (see Table II). Finally, the molar anionic charge densities Θ of AFS and FLA are obtained according to $\Theta = \varepsilon_m/V$. The results are shown in Table III. As was expected, the molar anionic charge density of AFS becomes lower with decreasing DS. The difference is particularly large between the AFS polymers containing 0.5 and 0.4 mol of sulfite per mol acetone, indicating that with respect to adsorption tendency, the highest sulfonated AFS differs significantly from the rest of the AFS polymers possessing lower DS. It is also shown that the AFS polymer containing 0.2 mol of sulfite

TABLE IV
Adsorbed Amount and Rheology (Shear Stress) of Cement Slurries Containing 0.2% bwoc of Different
AFS Samples Measured at Different Shear Rates

Molar ratio of acetone : formaldehyde : sulfite	Shear stress (lbs/100 ft^2) at different shear rates						Adsorbed amount of AFS (mg/g cement)
	600 rpm	300 rpm	200 rpm	100 rpm	6 rpm	3 rpm	
1 : 3 : 0.5	72	40	34	26	14	12	1.4
1 : 3 : 0.4	90	58	48	37	19	13	1.2
1 : 3 : 0.3	95	62	53	41	21	13	1.0
1 : 3 : 0.2	113	77	61	53	22	14	0.9
Without AFS	>300	202	150	93	14	10	–
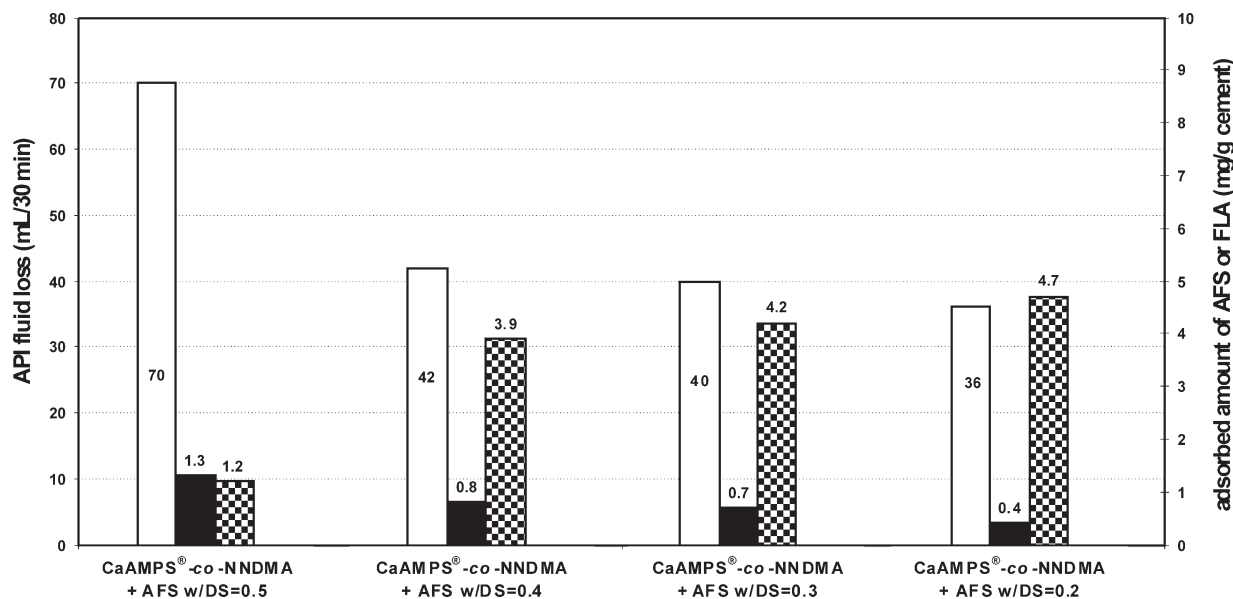
Figure 3 API fluid loss (white bars) and adsorbed amount of AFS (black bars) and FLA (dotted bars) of cement slurries containing AFS samples synthesized with different degrees of sulfonation (dosages: FLA 0.5% bwoc, AFS 0.2% bwoc).

per mol of acetone practically possesses the same molar anionic charge density as FLA.

Table IV shows the rheological properties of the cement slurry prepared with 0.2% by weight of cement (bwoc) of the different AFS samples. The measured shear stress represents the effectiveness of the AFS. The lower the shear stress at a given shear rate, the more effective is the AFS dispersant. The dispersing effectiveness of AFS decreases when DS abates. At the same time, the adsorbed amount of AFS decreases as well. Thus, it is evident that the adsorption behavior of AFS is controlled by its molar anionic charge density which derives from its DS.

AFS behavior in the presence of FLA

For combinations of 0.2% bwoc of synthesized AFS samples with 0.5% bwoc FLA, the API fluid loss, adsorbed amount, and cement slurry rheology of each combination were measured. API fluid loss represents the effectiveness of the FLA. The lower the value, the more effective is the FLA. Figure 3 shows

that the API fluid loss generally decreases when the molar amount of sulfite in the dispersant is reduced from 0.5 to 0.2 mol per mol acetone. The biggest improvement in API fluid loss is achieved when DS of AFS is reduced from 0.5 to 0.4. At even lower DS (0.3 and 0.2, respectively), API fluid loss drops only slightly. This result correlates well with the differences in molar anionic charge densities of the AFS polymers (see Table III). There, the greatest difference exists between the AFS samples with 0.5 and 0.4, respectively, too. Probably, the molar anionic charge density is the critical parameter which determines the adsorption behavior of the polymers relative to each other. The lower DS causes dispersant adsorption to decline from 1.3 (0.5 mol sulfite) to 0.4 mg/g cement (0.2 mol sulfite). Simultaneously, it allows adsorption of the FLA to increase from 1.2 to 4.7 mg/g cement. As the adsorbed amount of AFS polymer decreases, the electrostatic repulsion between solid particles diminishes which produces a slightly higher viscosity of the cement slurries (see Table V). The rheology data demonstrate that,

TABLE V
Rheology (Shear Stress) of Cement Slurries Containing 0.2% bwoc of Synthesized AFS Samples and 0.5% bwoc FLA, Measured at Different Shear Rates

Molar ratio of acetone : formaldehyde : sulfite	Shear stress (lbs/100 ft^2) at different shear rates					
	600 rpm	300 rpm	200 rpm	100 rpm	6 rpm	3 rpm
1 : 3 : 0.5	252	146	106	60	6	4
1 : 3 : 0.4	275	158	114	65	6	3
1 : 3 : 0.3	285	167	121	69	6	3
1 : 3 : 0.2	295	171	124	71	6	3
Without AFS	>300	202	150	93	14	10
With FLA only	293	178	133	81	11	8

of all synthesized AFS samples, the polymer with DS = 0.4 shows the strongest dispersing effect. In combination with FLA, it produces excellent fluid loss control of the slurry while slurry rheology remains low. Thus, when both FLA and dispersant compete for the limited number of adsorption sites on cement surface, CaAMPS-*co*-NNDMA is no longer displaced from the surface when an AFS with a lower DS is used as a dispersant.

CONCLUSIONS

The performance of multi-admixture systems can be lower than the added effects of each single component present in the system. This phenomenon is commonly referred to as admixture incompatibility. For technical and economical reasons it is important to understand the mechanism behind this effect.

This study shows that when adsorption is the principle process determining admixture effectiveness, admixture incompatibility can develop because a strongly adsorbing component may reduce or even prevent adsorption of the other admixtures. In the case of AFS dispersant and CaAMPS-*co*-NNDMA FLA it was found that a surprisingly minor adjustment of the DS and, consequently, of the molar anionic charge density of AFS dispersant relative to CaAMPS-*co*-NNDMA FLA enables both admixtures to adsorb simultaneously and to develop their full performance potential. This principle behavior generally applies to superplasticizers based on polycondensation chemistry. In experiments not discussed here we confirmed that differently sulfonated melamine formaldehyde sulfite polymers behave similar to AFS, i.e., their DS determines the performance in combination with CaAMPS-*co*-NNDMA FLA. For other admixture combinations, additional parameters determining their adsorption behavior, such as steric position of the anchor groups along the main chain, adsorbed conformation of the macromolecule, and enthalpic and entropic effects, may be considered as

well to develop solutions. The insight into the working mechanism of admixtures and the processes occurring at the surface of colloid particles allows to optimize multi-admixture systems through specific molecular engineering and to eliminate the well-known phenomena of admixture incompatibility.

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