Adsorption Behavior and Effectiveness of Poly(*N*,*N*-dimethylacrylamide-*co*-Ca 2-acrylamido-2-methylpropanesulfonate) as Cement Fluid Loss Additive in the Presence of Acetone-Formaldehyde-Sulfite Dispersant

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ABSTRACT: A copolymer of *N*,*N*-dimethylacrylamide and Calcium 2-acrylamido-2-methylpropanesulfonate was synthesized by free-radical copolymerization. Its performance as anionic fluid loss additive (FLA) was studied by measuring static filtration properties of oil well cement slurries at 27°C and 70 bar pressure, respectively. It was found that cement filter cake permeability and API fluid loss decrease with increasing FLA dosage. Filtrate analysis revealed a linear correlation between fluid loss and the amount of FLA adsorbed on the cement surface. FLA adsorption on cement was determined by total organic carbon (TOC) analysis in cement filtrate and confirmed by ζ-potential measurement. According to environmental scanning electron microscopy (ESEM) investigations, FLA does not alter the filter cake structure. In the presence of an anionic acetone–formaldehyde–sulfite (AFS) polycondensate dispersant, fluid loss control from FLA decreased and cement filter cake permeability increased because AFS reduces the amount of FLA adsorbed. In comparison to FLA, AFS shows stronger adsorption on the cement surface and succeeds in the competition with FLA. The different adsorption behavior of the two polymers is the reason for limited compatibility of this admixture com bination. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4341–4347, 2006

Key words: water-soluble polymer; polyelectrolytes; fluid loss additive; oil well cement; adsorption

INTRODUCTION

Oil or gas well cementing is routinely performed to achieve zonal isolation and to provide a stable and safe well-bore.[1] The process requires chemical admixtures to optimize cement slurry properties. For example, premature dehydration of the cement slurry pumped along the porous formation can result in poor slurry properties (e.g., high viscosity, short thickening time, etc.) or even in complete failure. Fluid loss additives (FLAs) are added to the cement to prevent water loss from the slurry.[2,3] The introduction of high-temperature stable, synthetic, water-soluble FLA polymers allowed to cement ultra-deep wells with temperatures ranging up to 260°C.[4] Copolymers of *N*,*N*-dimethylacrylamide (NNDMA) with sulfonated monomers, particularly the Ca salt of 2-acrylamido-2-methylpropanesulfonic acid (AMPS®), were found to be effective anionic FLAs for well cementing.[5,6] According to the work published by Desbrieres in 1993,[7] anionic or nonionic FLAs reduce filter cake permeability of cement slurries. To accomplish this, three mechanisms may be considered: first, adsorption of large macromolecules on cement may decrease the effective pore diameter; second, plugging of the pore constriction by the hydrated and swollen polymers in solution; and third, modification of the cake structure, e.g., increasing its compaction. To this date, no scientific evidence exists about the contribution of each of these mechanisms.[3,7,8]

Therefore, a test program was performed to determine the primary working mechanism of poly-(NNDMA-*co*-CaAMPS®)-based FLA. Static fluid loss properties of cement slurries containing different FLA dosages and polymer adsorption on cement were measured to determine whether there was a correlation between these two parameters. Potential FLA adsorption was also studied by ζ-potential measurement. Environmental scanning electron microscope (ESEM) pictures of fresh filter cakes with and without FLA were taken to show the possible changes in the filter cake structure. Fluid loss control of cement slurries containing the anionic FLA and an acetone–formaldehyde–sulfite (AFS) dispersant and adsorption of

TABLE I
Characteristics of Anionic Fluid Loss Additive (FLA) and Anionic Dispersant (AFS)

Polymer	Molecular weight, M_w (g/mol)	Molecular weight M_n (g/mol)	Polydispersity, M_w/M_n	Radius of gyration, Rg_w (nm)	Anionic charge density ε of polymer in cement filtrate (C/g)
FLA	1,831,000	1,201,000	1.5	70.3	337
AFS	112,500	19,730	5.7	10.5	321

each admixture in the combination were investigated. The interaction between these two admixtures and the role of FLA adsorption for fluid loss control of the cement slurry are described.

EXPERIMENTAL

Synthesis and characterization of FLA

Copolymers of NNDMA and AMPS were prepared in the laboratory. To remove the stabilizers, NNDMA obtained from Sigma-Aldrich Chemical Co. (Munich, Germany) was exposed over calcium hydride for about 24 h and then distilled under vacuum. AMPS was obtained from Merck-Schuchardt (Darmstadt, Germany) and ammonium persulfate was obtained from Sigma-Aldrich Chemical Co. Synthesis procedures of acrylamide copolymers are well established.[9,10] NNDMA-co-CaAMPS® was prepared by aqueous solution polymerization technique using a persulfate initiator. In a three-necked, 2-L round-bottom flask, the monomers (molar ratio AMPS : NNDMA = 1 : 0.63) were dissolved in degassed, distilled water to give a 12.0 wt % solution. Nitrogen gas was bubbled through the reaction mixture for 30 min at 25°C with slow stirring. After heating to 60°C, 0.15% (by weight of monomer) ammonium persulfate in aqueous solution was added drop-wise to the reaction mixture. The reaction flask was kept at 60°C for 2 h with constant stirring of the solution. During polymerization, the reaction mixture became viscous. The solution was diluted with water three times its volume and neutralized with 2% Ca(OH)$_2$ solution. The polymer solution had a solid content of 4.1 wt %, determined by infrared balance (Sartorius, Germany).

The molecular weight (M_w and M_n) of FLA was determined by gel permeation chromatography (GPC) using 0.2M NaNO$_3$ aqueous solution (adjusted with NaOH to pH 9) as an eluent at a flow rate of 1.0 mL/min. FLA solution was filtered through a 5-μm filter. Polymer solution was measured on Waters Alliance 2695 using two Aquagel-OH 60 columns from Polymer Laboratories with RI-detector 2414 (Waters) using $dn/dc = 0.156$ mL/g (value for polyacrylamides)[11] and an 18 angle dynamic light scattering detector (Wyatt Dawn EOS, Wyatt Technologies).

The anionic charge amount of FLA was determined by charge titration with a PCD 03 pH (Mütek Analytic, Germany) using poly(diallyl-dimethyl-ammonium-chloride) as cationic polyelectrolyte. The properties of FLA are listed in Table I.

Synthesis and characterization of AFS

Synthesis of AFS polycondensate was carried out according to Aignesberger and Plank.[12,13] In a jacketed 2-L reactor flask equipped with a baffle stirrer and a reflux condenser, acetone and sodium bisulfite at a molar ratio of 1 : 0.5 were dissolved in water. When sodium bisulfite was dissolved, the temperature of the solution had increased to 32°C. As soon as the solution became clear, the temperature was raised to 56°C. From a dropping funnel an aqueous 30% formaldehyde solution was fed into the reactor at a molar ratio between acetone and formaldehyde of 1 : 3. During the feeding process, heat from the exothermic reaction causes the temperature to increase further. Cooling was used to maintain a temperature of 60–70°C. After the feeding of formaldehyde was finished, the temperature was raised to 90–95°C and continued for another 1 h. After cooling, the polycondensate solution had a solids content of 33.8 wt %, determined by infrared balance.

The molecular weight (M_w and M_n) of AFS was determined with GPC measurement (Table I). The

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

C_3S (wt %)	C_2S (wt %)	C_3A_c (wt %)	C_4AF (wt %)	Free CaO (wt %)	$CaSO_4 \cdot 2H_2O$ (wt %)	$CaSO_4$ (wt %)	Specific density (kg/L)	Specific surface area (m^2/kg)	d_{50}-Value (μm)
59.6	22.8	1.2	13.0	< 0.3	2.7	0.7	3.18	305.8	9.8

polymer was analyzed using 0.1M NaNO$_3$ aqueous solution (adjusted with NaOH to pH 12) as an eluent at a flow rate of 1.0 mL/min. The AFS solution was filtered through a 0.2-μm filter and measured on Alliance 2695 (Waters) using Ultrahydrogel 500, 250, 120 columns (Waters) with RI-detector 2414 (Waters) using $dn/dc = 0.135$ mL/g (value for poly(ethylene oxide))[14] and a 3 angle dynamic light scattering detector (Wyatt Dawn EOS).

The anionic charge amount of AFS was determined by charge titration with a PCD 03 pH and poly (diallyl-dimethyl-ammonium-chloride) as cationic polyelectrolyte. The properties of AFS are listed in Table I.

Cement slurry preparation

Cement slurries were prepared according to API Specification 10 B using, API Class G oil well cement and deionized water.[15] The cement slurry was mixed at a water-to-cement ratio of 0.44 by weight of cement (bwoc) using a Waring blender. To ensure homogeneous consistency, all slurries were prepared at ambient temperature and then stirred in an atmospheric consistometer at 27°C for 20 min. The phase composition, specific density, and specific surface area of the oil well cement are presented in Table II.

Static fluid loss and parameters for the filtration equation

Static fluid loss was determined following API RP 10B procedure using a high-temperature high-pressure filter press at 70 bar differential pressure and 27°C. The fluid volume collected within 30 min (V_{30}) was doubled as described by API RP 10B and regarded as API fluid loss of the corresponding cement slurry. It represents the effectiveness of the FLA. The
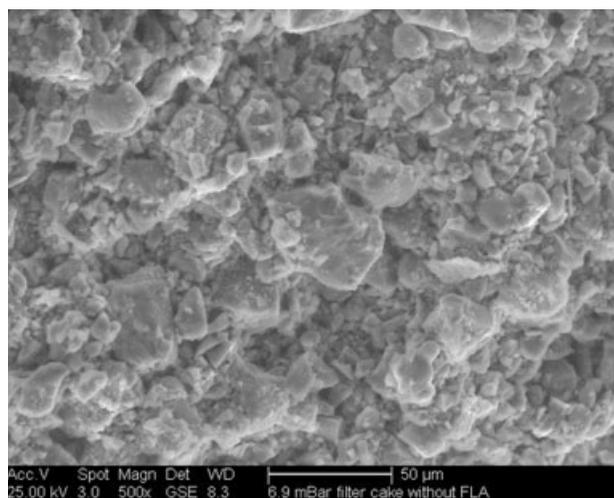
Figure 1 ESEM picture of filter cake from cement slurry without FLA (magnification: ×500).
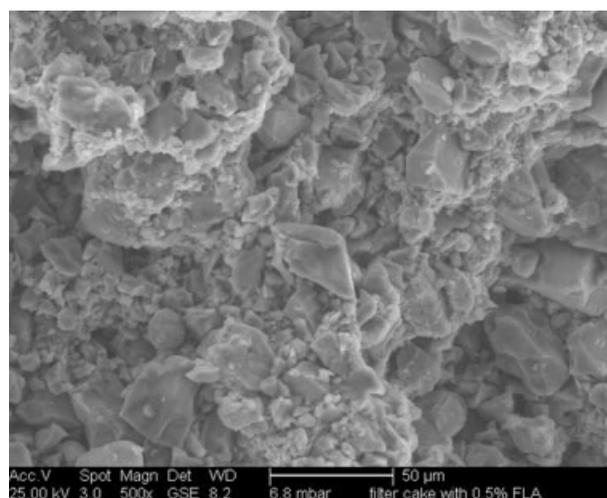
Figure 2 ESEM picture of filter cake from cement slurry with 0.5 by wt % of cement FLA (magnification: ×500).

lower the fluid loss, the more effective is the FLA. Dynamic viscosity, η, of the filtrate obtained was calculated from the kinematic viscosity (measured by Ubbelohde viscosimeter) and specific density. The reduced filter cake volume, R, was calculated from the ratio of cake volume and filtrate volume.

Environmental scanning electron microscopy

The fresh filter cake from the fluid loss test was cut horizontally into two equal halves. The surface of the fragment which was inside the filter cake was investigated by an environmental scanning electron microscope (XL 30 ESEM FEG from FEI Germany) with a GSE-detector (accelerating potential 25.0 kV at 3°C and 6.8 mbar). The ESEM allows to view the wet filter cakes in their original, unaltered state.

Adsorption measurements

The adsorbed amount of admixture 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

$$V_t = \sqrt{\frac{2\,K\,A^2\,\Delta p}{\eta\,R}}\,\sqrt{t}$$

Figure 3 Calculation of filter cake permeability K from cement slurry filtrate volume V_t, filtration area A, static pressure difference Δp, dynamic viscosity of filtrate η, reduced filter cake volume R and filtration time t (after Desbrieres).[7,8]

TABLE III
API Fluid Loss, Reduced Filter Cake Volume, Dynamic Filtrate Viscosity, and Filter Cake Permeability of Cement Slurries as a Function of FLA Dosage

FLA dosage (wt %, bwoc)	API fluid loss at 70 bar and 27°C (mL/30 min)	Reduced filter cake volume, R	Dynamic filtrate viscosity, η (mPa s)	Filter cake permeability, K (μD)
0	1270 (calculated)	2.0	1.0	6366
0.1	1163 (calculated)	2.1	1.0	5551
0.2	500 (calculated)	2.1	1.2	1269
0.3	166	2.2	1.3	148
0.4	62	2.4	1.4	25
0.5	40	2.5	1.4	11
0.6	34	2.5	1.4	8.0
0.7	32	2.4	1.5	7.1
0.8	30	2.4	1.5	6.4
0.9	26	2.4	1.6	5.1
1.0	24	2.5	1.6	4.5

same values for adsorbed amount of polymers were found. Equilibrium was also confirmed by ζ-potential numbers which are constant at the time of collecting the filtrate for adsorption measurement. 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 FLA was present in the cement filtrate, its concentration was measured by total organic carbon (TOC) analysis (Elementar High TOC II with CO_2-detector). When both admixtures were present, FLA concentration was determined by TN analysis (Elementar High TOC II with NO-detector) and the sum of adsorbed FLA and AFS polymers by TOC analysis. To accomplish this, the alkaline cement filtrate obtained from the fluid loss test was adjusted to neutral pH by adding 0.01M phosphoric acid.

ζ-Potential measurements

For determination of ζ-potential, the prepared cement slurries were investigated with an electroacoustic analyzer (DT 1200, Dispersion Technology, New York). The particle size at 50 wt % (d_{50}-value) and the density of the cement, which are necessary for calculating the ζ-potential value, were determined with a laser granulometric analyzer (Cilas 1064, Cilas, Germany) and a pycnometer (Ultrapycnometer 1000T, Quantachrome, Germany), respectively (Table II).

RESULTS AND DISCUSSION

FLA influence on filter cake structure

Fresh filter cakes of the cement slurry without and with 0.5% bwoc FLA were investigated by ESEM and
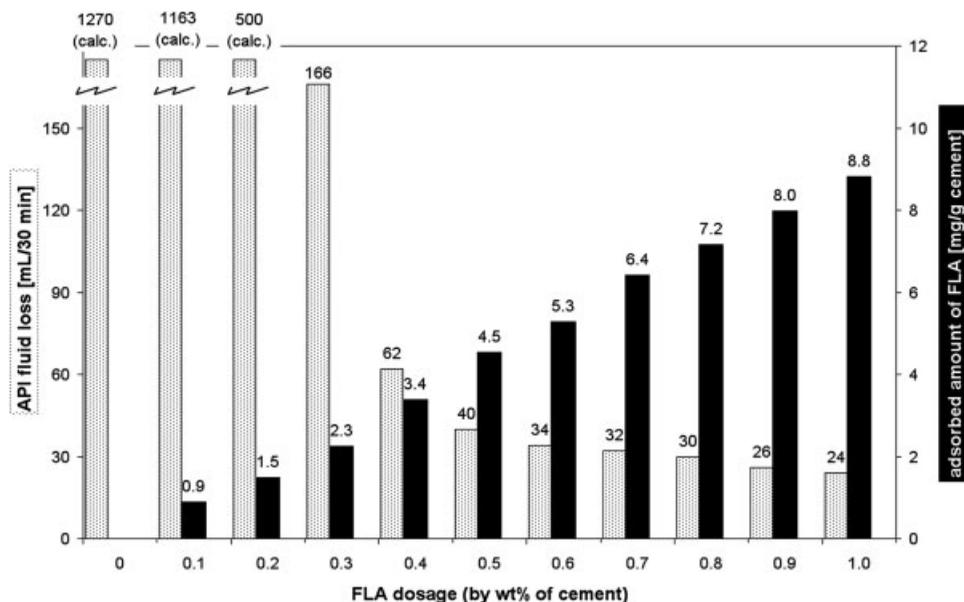

Figure 4 API fluid loss (white bars) and adsorbed amount of FLA (black bars) as a function of dosage.

$$\text{API fluid loss} = 2\,V_t\sqrt{\frac{30}{t}}$$

Figure 5 Calculation of API fluid loss from filtrate volume V_t (mL) collected up until dehydration (blow out) of cement slurry at the time t (min).[15]

compared (Figs. 1 and 2). No modification of the filter cake structure caused by FLA is recognizable. Packing and size of the hydrating cement particles as well as pore sizes in the filter cake are comparable. Since FLA does not modify the microstructure of the filter cake with respect to packing and size of hydrating cement particles, the effect of FLA on filter cake permeability as a potential mechanism for fluid loss control was studied.

Filter cake permeability

By using the simplified filtration equation derived from Desbrieres (Fig. 3) and inserting the measured filtrate viscosities η and reduced filter cake volumes R, filter cake permeabilities K for different FLA dosages were calculated.[7,8] The results are presented in Table III. Obviously, the major parameter for control of fluid loss from a cement slurry by FLA is the reduction in filter cake permeability. With increasing FLA dosage, the filtrate volume decreases, which confirms the effectiveness of FLA. At the same time, filter cake permeability is dramatically reduced by a factor of 1400 (from 6366 μD for the neat cement slurry to 4.5 μD for the slurry with 1.0% bwoc FLA). Filtrate viscosity of the filtrate rises only by a factor of 0.6 from 1.0 to 1.6 mPa s. It confirms Desbrieres's finding that the reduction of filter cake permeability is the

predominant reason for low fluid loss achieved by anionic FLA polymer in well cement.

Relationship between fluid loss and FLA adsorption

Static fluid loss volumes obtained within 30 min filtration time and the amounts of FLA adsorbed on cement were compared with increasing FLA dosage. As shown in Figure 4, API fluid loss decreases with increasing FLA dosage. For example, API fluid loss decreases from 1163 mL (calculated according to Fig. 5 from filtration volume obtained at dehydration of slurry) at 0.1% bwoc FLA to 24 mL for 1.0% bwoc FLA. At the same time, the corresponding adsorbed amount of FLA increases from 0.9 mg of polymer/g of cement for 0.1% bwoc to 8.8 mg of polymer/g of cement for 1.0% bwoc FLA. Therefore, the effectiveness of FLA correlates directly with its adsorbed amount. Obviously, the working mechanism of FLA is based on adsorption. The adsorption of FLA on hydrating cement particles is physical in nature and is based on electrostatic interaction between the negative $-SO_3^-$ groups of the anionic polymer and the positive Stern layer of the hydrating cement particle.[16,17] About 90% of FLA added to the slurry adsorb, indicating a high adsorption tendency of FLA on cement. FLA dosages > 1.0% bwoc were not tested. At these dosages, the cement slurry becomes too thick to mix. Therefore, no data at FLA dosages beyond 1.0% bwoc are available.

The adsorption of anionic FLA on the hydrating cement surface is confirmed by increasingly negative ζ-potential of the cement slurry with increasing FLA dosage (Fig. 6).
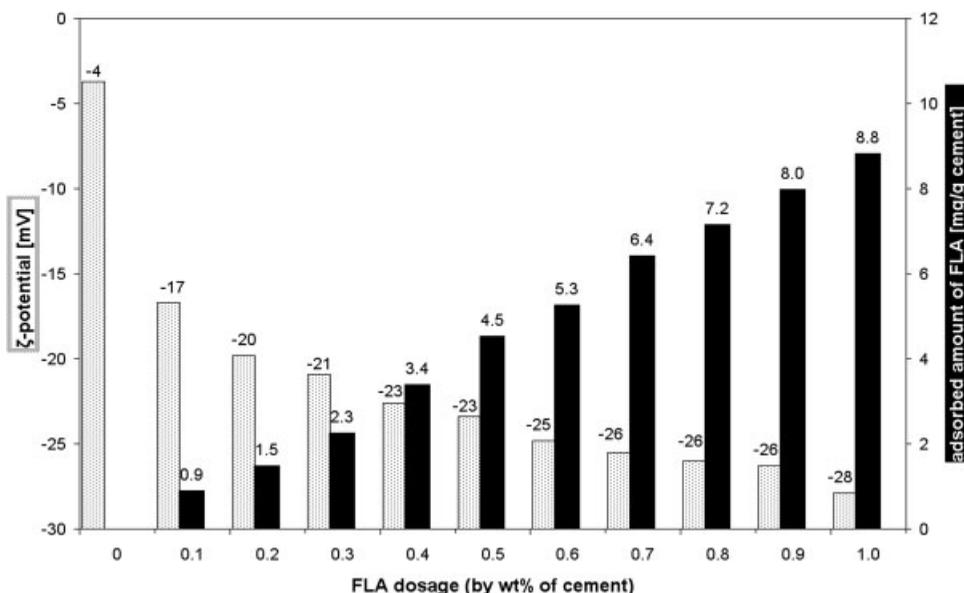
Figure 6 ζ-Potential of cement slurry (white bars) and adsorbed amount of FLA (black bars) as a function of dosage.
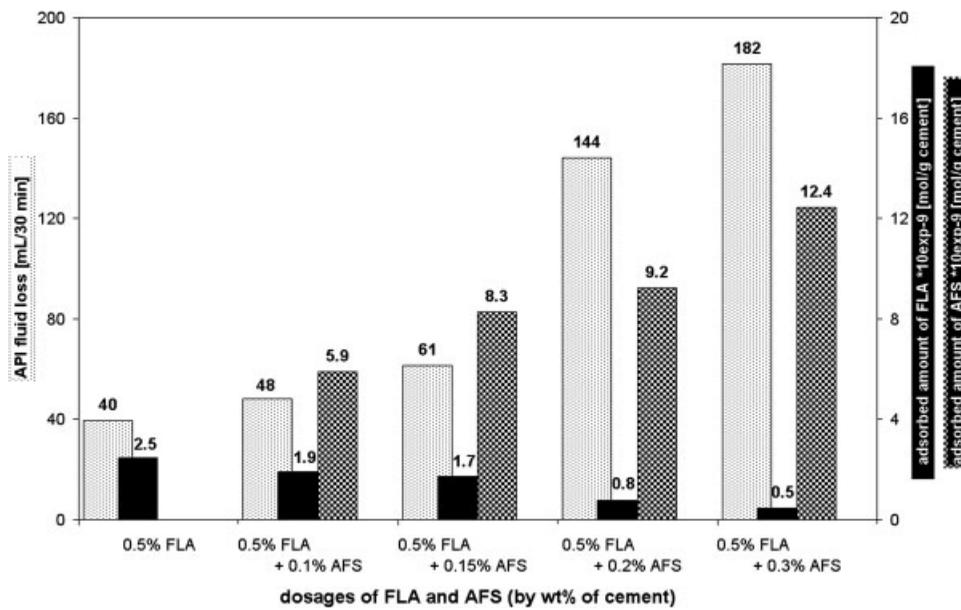
Figure 7   API fluid loss (white bars) and adsorbed amount of FLA (black bars) and AFS dispersant (dotted bars), respectively, as a function of dosage.

Fluid loss, FLA adsorption, and cement filter cake permeability in the presence of AFS dispersant

Cement slurries containing 0.5% bwoc FLA and different AFS dosages (0%, 0.1%, 0.15%, 0.2%, and 0.3% bwoc) were investigated with respect to fluid loss reduction, FLA, and AFS adsorption. The results are shown in Figure 7. With increasing AFS dosage, API fluid loss increases from 40 mL (without AFS) to 182 mL for the binary admixture system containing 0.5% FLA and 0.3% AFS, respectively.

At the same time, the amount of adsorbed FLA on cement decreases with increasing AFS dosage from 2.5×10^{-9} mol FLA/g of cement for the slurry with 0.5% bwoc FLA and without AFS to 0.5×10^{-9} mol FLA/g of cement for the binary admixture system containing 0.5% bwoc FLA and 0.3% bwoc AFS, respectively. Reduced adsorption of FLA in the presence of AFS also results in an increase of the dynamic filtrate viscosity (Table V). FLA is a high-molecular-weight polymer which when unadsorbed causes filtrate viscosity to increase. The calculated molar anionic charge density of AFS is significantly higher than for FLA (Table IV). This is one major reason why AFS shows higher adsorption than FLA. Reduced FLA adsorption occurring with increasing AFS dosage explains the poor effectiveness of FLA in the presence of AFS. It also confirms the adsorptive working mechanism of FLA. Adsorption of AFS in the binary admixture system shows an increase in the amount of adsorbed AFS with increasing AFS dosage (5.9×10^{-9} mol AFS/g of cement for the slurry with 0.5% bwoc FLA and 0.1% bwoc AFS, respectively, and 12.4×10^{-9} mol AFS/g of cement for the system with 0.5% bwoc FLA and 0.3% bwoc AFS, respectively).

Table V demonstrates that filter cake permeability of the cement slurry containing both FLA and AFS increases with increased AFS dosage. It confirms that the adsorbed amount of FLA determines filter cake

TABLE IV
Calculation of Anionic Charge Density for Anionic Fluid Loss Additive (FLA) and Anionic Dispersant (AFS)

Polymer	Molar anionic charge amount, ε_m (10^6) (C/mol)[a]	Molecule radius, R (nm)[b]	Molecule volume, V (nm^3)[c]	Calculated molar anionic charge density, ρ (C mol^{-1} nm^{-3})[d]
FLA	617	90.8	3,135,784	197
AFS	36	13.6	10,537	3,427

[a] $\varepsilon_m = \varepsilon\, M_w$.
[b] $R = [(5/3)Rg_w^2]^{0.5}$ model : hard sphere.[18]
[c] $V = 4/3\pi R^3$.
[d] $\rho = \varepsilon_m / V$.

TABLE V
API Fluid Loss, Reduced Filter Cake Volume, Dynamic Filtrate Viscosity, and Filter Cake Permeability of Cement Slurries as a Function of FLA and AFS Dosage

Binary admixture system (wt %, bwoc)	API fluid loss at 70 bar and 27°C (mL/30 min)	Reduced filter cake volume, R	Dynamic filtrate viscosity, η (mPa s)	Filter cake permeability, K (μD)
0.5% FLA + 0.1% AFS	48	2.4	2.1	22
0.5% FLA + 0.15% AFS	61	2.3	2.9	50
0.5% FLA + 0.2% AFS	144	2.2	5.9	528
0.5% FLA + 0.3% AFS	182	2.0	8.8	1161

permeability, and thus, the fluid loss achieved from a cement slurry.

The reduced adsorption of FLA in the presence of AFS is attributed to a competition between both anionic polymers for limited adsorption area and electrostatic attraction on the surface of hydrating cement particles. Main factors influencing the adsorption behavior of a polyelectrolyte are molar charge density and conformation of the macromolecule, charge density in the adsorbing anionic anchor group, adsorption enthalpy, and entropic effects. In the case of FLA and AFS, their quite different molar masses have to be considered. AFS, with its low molar mass, can be expected to adsorb flat, resulting in a higher surface coverage than FLA with its larger coil dimensions.

CONCLUSIONS

Poly(NNDMA-*co*-CaAMPS) anionic FLA effectively reduces filter cake permeability of oil well cement. This is achieved by adsorption of the polymer on cement. Adsorption is confirmed by TOC in the cement filtrate and by ζ-potential measurement of the cement paste with FLA. ESEM pictures show that FLA does not change filter cake structure. A direct correlation between fluid loss control and FLA adsorption was found. It confirms the adsorptive working mechanism for FLA. Poor compatibility between anionic FLA and an anionic AFS dispersant is explained by competitive adsorption. Because of higher molar anionic charge density, AFS adsorbs in high amount, reduces FLA adsorption, and increases filter cake permeability. Further studies are underway to determine FLA compatibility with other oil well cement admixtures such as, e.g., lignosulfonate re-

tarders. The goal being to obtain a fundamental understanding of parameters impacting admixture compatibility and to establish guidelines for optimum compatibility, this should allow a more economical use of expensive admixtures such as, e.g., polymeric FLAs.

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