

Effect of High Temperature and the Role of Sulfate on Adsorption Behavior and Effectiveness of AMPS[®]-Based Cement Fluid Loss Polymers

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ABSTRACT: The fluid loss control performance of 2-acrylamido-2-methylpropane sulfonic acid (AMPS[®])-based copolymers added to cement slurries was studied at 27 and 100°C, respectively. It was found that effectiveness of these fluid loss additives solely relies on achievement of a high adsorbed amount on the surface of cement. At elevated temperature (100°C), CaAMPS[®]-*N,N*-dimethyl acrylamide copolymer (CaAMPS[®]-*co*-NNDMA) exhibits reduced adsorption and hence decreased fluid loss control of the cement slurry. The reason behind this behavior is poor calcium binding capability of the sulfonate anchor groups, which coordinate with calcium atoms present on the mineral surface. Whereas, an increase in the sulfate concentration present in cement pore solution instigates partial coiling of CaAMPS[®]-*co*-NNDMA and causes only a slight influence on the performance of this copolymer. The elevated sulfate content results from thermal degradation of ettringite, a cement hydrate mineral produced during the early stages of cement hydration.

Incorporation of minor amounts (~ 1.3 mol %) of maleic anhydride into this copolymer produces a terpolymer, which exhibits higher and more stable adsorption, even at high temperature. This effect is owed to the presence of homopolymer blocks of polycarboxylates distributed along the polymer trunk. On mineral surfaces, they present much stronger anchor groups than sulfonate functionalities, as evidenced by their higher calcium binding capability. Consequently, fluid loss performance of CaAMPS[®]-*co*-NNDMA-*co*-MA is little affected by temperature. Understanding the influence of temperature on the physicochemical interactions occurring between additives and the mineral surface can help to design more effective admixtures suitable for high temperature applications. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1086–1095, 2011

Key words: oil well cement; adsorption; AMPS[®] copolymer; water-soluble polymers; high temperature

INTRODUCTION

In oil well cementing, water-soluble copolymers are applied to produce cement slurries, which function at the demanding conditions occurring in wellbores such as high temperature, pressure, and salinity.^{1,2} Synthetic fluid loss additives (FLAs), particularly copolymers made from 2-acrylamido-2-methylpropane sulfonic acid and *N,N*-dimethyl acrylamide monomers (CaAMPS[®]-*co*-NNDMA), are used to prevent the loss of water from the cement slurry while being pumped along porous formations. Such anionic copolymers provide fluid loss control by reducing filter cake permeability through polymer adsorption onto the positively charged surfaces of cement hydrates (adsorptive working mechanism).^{3,4} Whereas when highly anionic dispersants such as acetone-formaldehyde-sulfite

(AFS) polycondensates are present in the cement slurry, CaAMPS[®]-*co*-NNDMA is prevented from adsorption. Instead, AFS occupies the surfaces of cement hydrates.⁵ Although this effect results in strong dispersion of cement, it instigates excessive water loss from the slurry. The phenomenon of competitive adsorption occurring between these two admixtures can be solved by incorporation of stronger anionic anchor groups into the FLA. This way, affinity of the two admixtures toward the mineral surface becomes more similar. Suitable anchor groups are those, which strongly chelate insufficiently coordinated calcium atoms present on the surface of cement hydrates. Consequently, a terpolymer made of 2-acrylamido-2-methylpropane sulfonic acid, *N,N*-dimethyl acrylamide, and a very small portion (~ 1.3 mol %) of maleic anhydride (CaAMPS[®]-*co*-NNDMA-*co*-MA) adsorbs in high amount and provides low fluid loss of the cement slurry, even in the presence of AFS dispersant.⁵

The forgoing tests were conducted at low temperature (27°C). Applicators of FLAs, however, are very familiar with the typically quite detrimental effect of elevated temperature on fluid loss. There, often

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

C ₃ S (wt %)	C ₂ S (wt %)	C ₃ A _c (wt %)	C ₄ AF (wt %)	Free CaO (wt %)	CaSO ₄ ·2H ₂ O (wt %)	CaSO ₄ ·1/2 H ₂ O (wt %)	CaSO ₄ (wt %)	Specific density (kg/L)	Specific surface area (cm ² /g)	d_{50} value (μm)
59.6	22.8	1.2	13.0	<0.3	2.7 ^a	0.0 ^a	0.7	3.18	3,058	9.8

C₃S, tricalcium silicate (Ca₃(SiO₄)O); C₂S, dicalcium silicate (Ca₂SiO₄); C₃A_c, cubic modification of tricalcium aluminate (Ca₃Al₆O₁₈); C₄AF, tetra calcium aluminate ferrite (Ca₄Al₂Fe₂O₁₀).

^a Measured by thermogravimetry.

substantially higher dosages of these costly admixtures are required to achieve a fluid loss, which is comparable with that at room temperature. So far, the causes behind this negative trend are not well understood. The main reason is that experiments with cement slurries at 100°C are very hard to conduct in the absence of a retarder. Under such conditions, a very careful test protocol has to be applied to be able to complete the fluid loss test before the set and hardening of cement begins, which can alter the test results. Solidification of the cement in the filtration cell also poses a severe health risk for the operator of the test and may result in a loss of the equipment.

Here, the aim of the study was to investigate the impact of high temperature (100°C) on the adsorption behavior and effectiveness of two AMPS[®]-based FLAs under carefully controlled experimental conditions. Namely, the fluid loss performances of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA were compared at 27 and 100°C, respectively. This way, an idea of the robustness of these two polymers under different temperature conditions was developed. To understand the mechanism underlying their effectiveness, adsorption of the two FLAs on cement and on silica, a cement slurry component, which is commonly used to prevent the strength retrogression of cement induced by high temperature, and their intrinsic viscosities in cement pore solutions were determined. Additionally, the radius of gyration of the copolymers was measured at different sulfate concentrations to investigate a potential impact of this anion on FLA performance. Finally, the calcium binding capability of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, were compared, and the data were used to explain the adsorption behavior of both polymers.

EXPERIMENTAL

Materials

Oil well cement

An API Class G oil well cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) correspond-

ing to American Petroleum Institute (API) Specification 10A was used.⁶ Phase composition, specific density, specific surface area (Blaine), and particle size (d_{50} value) of this cement sample are listed in Table I.

Silica flour

A commercial sample (SSA-1 from Halliburton, Celle, Germany) containing (wt %) quartz 97.60, CaO 0.57, MgO 0.18, Al₂O₃ 0.17, and TiO₂ 0.06 (determined by X-ray fluorescence analysis) was used. Its specific surface area (Blaine method) was 1,857 cm²/g. Its average particle size (d_{50} value) was 32.7 μm. Specific density of the silica flour was found at 2.65 kg/L.

AMPS[®] copolymers

First, the calcium salt of 2-acrylamido-2-methylpropanesulfonic acid-*co*-*N,N*-dimethyl acrylamide was synthesized by aqueous free radical copolymerization according to a process described in detail in the literature.^{5,7} This copolymer was designated CaAMPS[®]-*co*-NNDMA. The molar ratio between the AMPS[®] and NNDMA monomers was 1 : 0.63, and Na₂S₂O₈ was used as an initiator. Next, from AMPS[®], NNDMA, and maleic anhydride (MA) at monomer ratios of 1 : 0.63 : 0.02, a terpolymer was prepared following the same synthesis method. This terpolymer was designated CaAMPS[®]-*co*-NNDMA-*co*-MA. In all syntheses, laboratory grade AMPS[®] (2404 monomer from Lubrizol, Rouen, France), NNDMA and MA (supplied by Sigma-Aldrich, München, Germany) were used as obtained. Polymerizations were carried out at 60°C for 2 h providing odorless solutions possessing honey-like color and viscosity. Powdered samples of the AMPS[®] copolymers were obtained by dialysis and freeze drying. The chemical structures of the synthesized FLAs are presented in Figure 1, and their characteristic properties are summarized in Table II. The Burchard parameters calculated from the Rg_z/Rh_z values indicate that both copolymers possess a linear conformation, which is best described as an extremely stiff chain.⁸ Additionally, the copolymers

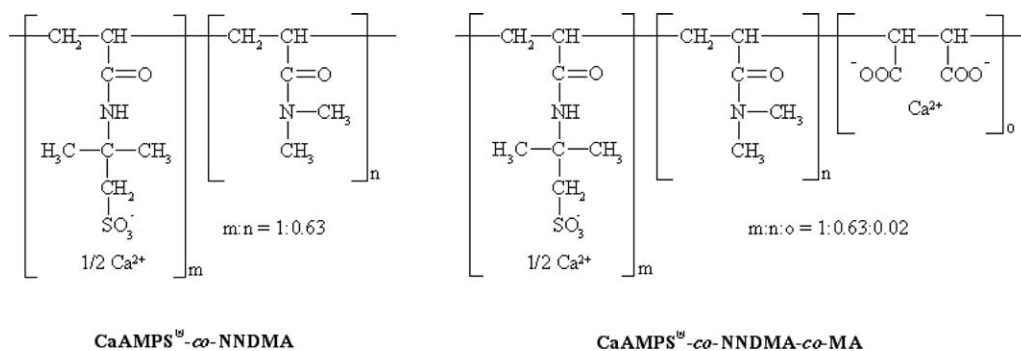


Figure 1 Chemical structures of the synthesized AMPS[®]-based copolymers.

were characterized by Brookfield viscosimetry, ¹H-NMR, and IR spectroscopy. At a concentration of 18 wt %, the copolymer solutions exhibited viscosities of 10,000 mPa·s for CaAMPS[®]-*co*-NNDMA and 7,000 mPa·s for CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively. The ¹H-NMR spectrum of CaAMPS[®]-*co*-NNDMA is presented in Figure 2. It shows proton resonances at $\delta = 1.3$ (a_1, a_3, b_1), 2.0 (a_2), 2.5 (b_2), and 3.0 ppm (a_4, b_3). The IR spectrum of this copolymer displays a N—H and O—H stretching band at 3319 cm⁻¹, a C=O stretching band at 1612 cm⁻¹, a N—H bending band at 1542 cm⁻¹, a C—H bending band of geminal dimethyl groups at 1405 cm⁻¹, S=O stretching bands at 1177 and 1038 cm⁻¹, and a S=O stretching band at 621 cm⁻¹ (see Figure 3). For CaAMPS[®]-*co*-NNDMA-*co*-MA identical ¹H-NMR and IR spectra were obtained. Obviously, incorporation of only 1 wt % of MA into the copolymer is too small an amount to be detected.

Instruments and procedures

Cement characterization

Phase composition of the cement sample was obtained by X-ray powder diffraction using a Bruker axs D8 Advance instrument from Bruker, Karlsruhe, Germany with Bragg-Bretano geometry. Topas 3.0 software was used to quantify the amounts of individual phases present in the sample by following

Rietveld's method of refinement.⁹ The instrument is equipped with a scintillation detector using Cu K_α ($\lambda = 1.5406 \text{ \AA}$) radiation with a scanning range between 5° and 80° 2 θ . Specific density of the cement sample was measured on an Ultracycrometer[®] 1000 (Quantachrome Instruments, Boynton Beach, FL). The specific surface area of the samples was determined with a Blaine instrument (Toni Technik, Berlin, Germany). The average particle size (d_{50}) was obtained from a laser-based particle size analyzer (1064 instrument from Cilas, Marseille, France).

Silica flour characterization

Oxide composition of the silica sample was determined using an X-ray fluorescence spectrometer (Axios from PANalytical, Almelo, Holland). Specific density, specific surface area, and average particle size (d_{50}) of the silica sample were measured using the same instruments as described above for cement.

Polymer characterization

Size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn, Germany) equipped with RI detector 2414 (Waters, Eschborn, Germany) and an 18 angle dynamic light scattering detector (Dawn EOS from Wyatt Technologies, Clinton, IA)

TABLE II
Characteristic Properties and Anionic Charge Amount of Synthesized Fluid Loss Polymers

FLA polymer	Molecular weights		Poly-dispersity index M_w/M_n	Radius of gyration, R_{gz} (nm)	Hydrodynamic radius, R_{hz} (nm)	Anionic charge amount, ϵ (C/g) ^a
	M_w (g/mol)	M_n (g/mol)				
CaAMPS [®] - <i>co</i> -NNDMA	2.0×10^6	1.2×10^6	1.7	64	7	377
CaAMPS [®] - <i>co</i> -NNDMA- <i>co</i> -MA	1.8×10^6	1.0×10^6	1.8	58	7	380

^a Measured in cement pore solution collected at 27°C.

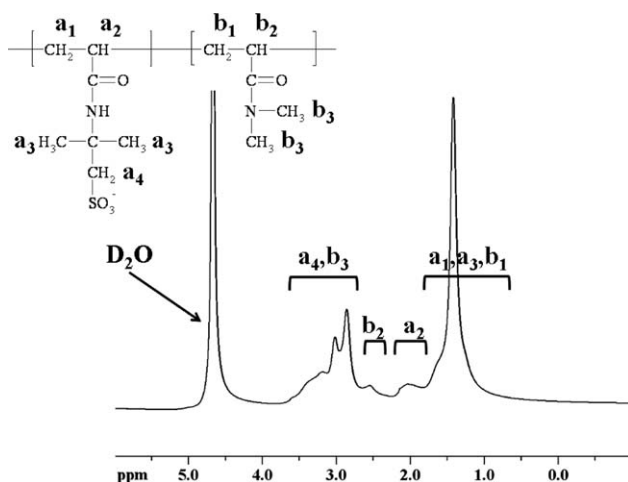


Figure 2 $^1\text{H-NMR}$ spectrum of CaAMPS[®]-*co*-NNDMA, measured in D_2O .

was used. The FLAs were separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). Molecular weights (M_w and M_n) and radii (R_{gz} and R_{hz}) of the FLAs were determined using a 0.2M aqueous NaNO_3 solution (adjusted with NaOH to pH 9) as an eluent at a flow rate of 1.0 mL/min. R_{gz} was measured at two different sulfate concentrations (6.8 and 8.3 g/L, respectively) present in the eluent by adding the appropriate amounts of Na_2SO_4 . The value of dn/dc used to calculate M_w and M_n was 0.156 mL/g (value for polyacrylamides).¹⁰ Thus, the molecular weights measured are relative to polyacrylamide.

Viscosity of the polymer solutions was determined at room temperature with a Brookfield viscometer (Model HA from Brookfield Engineering Labs, Middleboro, USA) equipped with #7 spindle at 100 rpm. By multiplying the dimensionless reading with the correspondent factor, the viscosity (mPa·s) was obtained.

Infrared spectra were measured with an attenuated total reflectance Fourier transform spectrophotometer (ATR-FTIR) (Vertex 70 from Bruker Optics, Karlsruhe, Germany). Each spectrum was acquired in transmittance mode on a Diamond ATR crystal cell (MPV-Pro from Harrich Scientific Products, Pleasantville, NY) by accumulation of 64 scans with a resolution of 4 cm^{-1} and a spectral range of $4000\text{--}350\text{ cm}^{-1}$. Moreover, powder samples of the synthesized fluid loss polymers were dissolved in D_2O , and $^1\text{H-NMR}$ spectra were taken at 300 K using a JNM-GX 400 spectrometer (JEOL GmbH, Eching, Germany).

The specific anionic charge amounts of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, were determined in 0.1M NaOH (pH 12.6) in presence or absence of calcium ions (0.6 g/L Ca^{2+} , added as $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$), or in cement pore solution at

room temperature using a PCD 03 pH apparatus (BTG Müttek GmbH, Herrsching, Germany). Charge titration was carried out according to a literature description using a 0.001N solution of laboratory grade poly(diallyl dimethylammonium chloride) from BTG Müttek GmbH, Herrsching, Germany as cationic polyelectrolyte.¹¹ Intrinsic viscosity of the polymers dissolved in cement pore solution was determined at 80°C using an Ubbelohde capillary viscometer (50110/I from Schott, Mainz, Germany). For this purpose, the flow time t of the polymer solution through the capillary was measured. From this, the kinematic viscosity ν was calculated according to $\nu = K(t - \zeta)$, where K is the viscometer constant ($0.1004\text{ mm}^2/\text{s}^2$) and ζ is the flow time dependent Hagenbach-Couette correction term. Multiplying the kinematic viscosity with the specific density ρ of the polymer solution produces the value for the dynamic viscosity η_{dyn} . From this, the reduced viscosity η_{red} was calculated according to $\eta_{\text{red}} = \frac{\eta_{\text{dyn}} - \eta_0}{\eta_0 \cdot c}$, where η_0 is the dynamic viscosity of the cement pore solution, and c represents the respective concentration of the dissolved polymer. Finally, the intrinsic viscosity η_{intr} is obtained from the intercept point of $\eta_{\text{red}} = f(c)$ with the y -axis when the polymer concentration c is extrapolated to 0. Under given conditions, the maximum deviation was found to be $\pm 0.01\text{ L/g}$.

Thermal stability of the AMPS[®] copolymers was investigated by thermogravimetry using a NETZSCH STA 409 CD instrument (NETZSCH-Gerätebau GmbH, Selb, Germany) in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The results are presented in Table III. Both copolymers first release residual water at 100°C before thermal decomposition begins at 330°C for CaAMPS[®]-*co*-NNDMA and at 337°C for CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively.

Cement slurry preparation

Cement slurries were prepared in accordance with the procedures set forth in Recommended Practice for Testing Well Cements, API Recommended

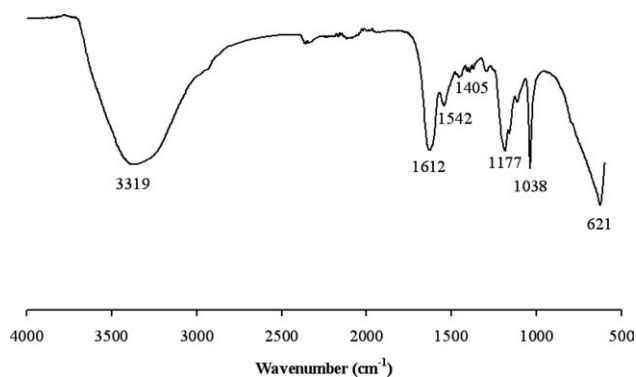


Figure 3 Powder FTIR spectrum of CaAMPS[®]-*co*-NNDMA.

TABLE III
Thermal Decomposition Behavior of Synthesized AMPS[®] Copolymers

FLA polymer	First stage		Second stage		Residual weight at 550°C (%)
	T_{\max} (°C)	wt loss (%)	T_{\max} (°C)	wt loss (%)	
CaAMPS [®] - <i>co</i> -NNDMA	330	32	385	14	35
CaAMPS [®] - <i>co</i> -NNDMA- <i>co</i> -MA	337	31	387	15	38

Practice 10B, issued by the API.¹² The slurries were mixed at a water-to-cement ratio of 0.44 using a blade-type laboratory blender manufactured by Waring Products (Torrington, CT). The synthesized FLAs were dissolved in deionized water to provide a polymer concentration of 11.36 g/L. This concentration corresponds to a dosage of 0.5% polymer by weight of cement (bwoc). The cement was added within 15 s to the aqueous polymer solution at a stirring speed of 4,000 rpm and mixed for 35 s at 12,000 rpm. To ensure homogeneous consistency, all slurries were stirred for 20 min at 27°C and 95°C, respectively, in an atmospheric consistometer (model 1250 from Chandler Engineering, Tulsa, OK).

Fluid loss test

Static fluid loss was measured at 27 and 100°C, respectively, using a 500-mL high-temperature high-pressure (HTHP) stainless steel filter cell manufactured by OFI Testing Equipment (Houston, TX). Design of this HTHP filter cell and its operation are described in detail in a norm issued by the API.¹² After pouring the homogenized slurry obtained from the consistometer into the HTHP cell, a heating jacket was used to adjust the test temperature. Then, a differential pressure of 70 bar N₂ was applied at the top of the cell. Filtration proceeded through a 3.5 sq. in. mesh metal sieve placed at the bottom of the cell. For measurements at 100°C, a steel condenser was used to convert the partially gaseous filtrate into its liquid state. The fluid volume collected within 30 min (V_{30}) was doubled as described by API RP 10B and designated as API fluid loss of the corresponding slurry. The values reported for the respective API fluid loss test represents the average obtained from three separate measurements. The maximum deviation was found at ± 10 mL/30 min.

Before conducting the filtration tests at 100°C, liquidity of the cement slurry over the entire test period of ~ 70 min had to be ensured by probing its thickening time on an HTHP consistometer (model 8240 from Chandler Engineering, Tulsa, OK). This instrument is capable of measuring the consistency (viscosity) of cement pastes under con-

ditions of high temperature (up to 315°C) and high pressure (up to 2750 bar). Slurry viscosity is measured in Bearden units of consistency (BC), a dimensionless unit obtained from the torque of a paddle rotating in the hydrating cement slurry, with no direct conversion factor to common units for viscosity. In this test, setting and solidification of cement is evidenced by an increase of slurry viscosity from <20 BC for the liquid paste to a value of 70 BC and higher. At this point, the curing cell has to be depressurized, cooled, and dismantled immediately to avoid destruction of the equipment. A value of 70 BC is generally considered to be the maximum pumpable consistency. In our study, the test protocol as follows was applied: The cement slurry containing 0.5% CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, was mixed in the Waring blender and immediately transferred into the cell of the HTHP consistometer. There, it was heated in a ramp-mode to 100°C and pressurized with 70 bar (heating rate 1.5°C/min; pressure rate 2.3 bar/min). Under those conditions, thickening times of 90 min were obtained, that is, the slurries remained fluid (<20 BC) for 80 min and reached 70 BC after a total curing time of 90 min. This time span was deemed to be sufficient to allow safe operation of the HTHP filtration tests at 100°C. Additionally, it ensured that low fluid loss values obtained at 100°C were not originating from premature setting and hardening of the cement paste in the HTHP filtration cell.

Analysis of cement pore solution

Pore solutions of cement slurries prepared without polymer addition were produced by HTHP filtration at 27 and 100°C, respectively. Under the latter conditions, again a condenser was used to prevent evaporation of water, which would result in higher than actual ion contents. Concentrations of cations present in the pore solutions were determined by atomic absorption spectroscopy (1100 B instrument from Perkin Elmer, Waltham, MA). The content of anions was measured using ion chromatography (ICS-2000 apparatus from Dionex, Idstein, Germany). Here, the alkaline cement filtrate was adjusted to pH 7 by adding 0.1M HCl.

Silica slurry preparation

Silica slurries were prepared following the same procedure described for the preparation of cement slurries, with the distinction that as mixing water, the cement pore solutions obtained at 27 and 100°C, respectively, were used instead of deionized water.

Polymer adsorption

The amount of admixture adsorbed on cement and silica, respectively, was determined from the filtrate collected in the fluid loss test. Generally, the depletion method was applied, that is, it was assumed that the decrease in the polymer concentration before and after contact with cement was solely due to the adsorption on the mineral surface. Achievement of adsorption equilibrium was confirmed by zeta potential measurement, which was stable at the time of collecting the filtrate for adsorption measurement. Adsorbed amount of FLA was calculated from the difference in the equilibrium concentrations of the polymer present in the liquid phase before and after contact with the adsorbents. A High TOC II apparatus (Elementar, Hanau, Germany) equipped with a CO₂ detector was used to quantify polymer adsorption. For TOC analysis, the alkaline cement filtrate containing the unadsorbed polymers was adjusted to pH 1 by adding 0.1M HCl. Each test was repeated three times, and the average was reported as adsorbed amount. The maximum deviation was ±0.1 mg polymer/g cement. Adsorption was confirmed to be the sole reason for admixture depletion through a solubility test. A total of 11.36 g/L of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, were dissolved in cement pore solution and stored for 1 day. In each test, no precipitation of the FLAs was observed.

Adsorption of sulfate

Adsorption of sulfate anions on silica flour was quantified from the filtrate collected in the fluid loss test. The adsorbed amount was calculated from the difference in the concentrations of the anions present in the pore solution before and after contact with silica. Sulfate concentrations were determined by ion chromatography (ICS-2000 apparatus from Dionex, Idstein, Germany). Here, the alkaline cement filtrate was adjusted to pH 7 by adding 0.1M HCl.

Zeta potential

Zeta potentials of cement slurries were measured at room temperature on an electroacoustic spectrometer (DT-1200 from Dispersion Technology, Bedford Hills, NY). The slurries were prepared as described before at a water-to-cement (*w/c*) ratio of 0.44. As

zeta potentials were determined as a function of time (here 30 min), the respective cement slurry was poured into the cup of the spectrometer immediately after mixing. Measurement occurred without further homogenization in the atmospheric consistometer.

RESULTS AND DISCUSSION

Properties of synthesized FLAs

The results of the SEC measurements confirm that both FLA polymers possess comparable molecular weights, radii, and molar anionic charge amounts (Table II). Obviously, addition of such minor amounts of MA does not alter the polymerization process and the principle properties of the polymer. The only difference between CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA being the number and type of the anchor groups, and their steric arrangement of their anchor groups. Distribution of MA holding the additional carboxylate anchor groups along the backbone of the macromolecule is critical for the adsorbed conformation of CaAMPS[®]-*co*-NNDMA-*co*-MA.⁵ Owing to the *e* values of AMPS[®] and NNDMA, which are opposite in sign, these monomers show an alternating sequence along the polymer backbone. In contrast, as the *Q* and *e* values of MA and AMPS[®] are completely different (see Table IV), MA will preferentially undergo homo polymerization.¹³ Therefore, it can be concluded that MA forms blocks of homopolymer within the CaAMPS[®]-*co*-NNDMA-*co*-MA terpolymer.

Temperature-dependent interaction with cement

The relationship between API fluid loss and the amount of the FLAs adsorbed on cement was determined at 27 and 100°C, respectively. The results are exhibited in Figure 2. There, it becomes obvious that the adsorbed amount of CaAMPS[®]-*co*-NNDMA is reduced at high temperature (from 4.6 mg polymer/g cement at 27°C to 3.9 mg polymer/g cement at 100°C). Consequently, API fluid loss of the cement slurry increases from 40 mL/30 min at 27°C to 120 mL/30 min at 100°C. One potential reason for the decreased performance at high temperature is thermal degradation of the polymer. According to TGA

TABLE IV
Q and *e* Values of the Monomers Used for Preparation of the Fluid Loss Polymers¹³

Monomer	<i>Q</i>	<i>e</i>
AMPS [®]	0.39	0.22
NNDMA	0.41	-0.26
Maleic anhydride	0.86	3.69

measurements presented in Table III, thermal decomposition of the CaAMPS[®]-*co*-NNDMA commences at $\sim 330^\circ\text{C}$. This finding corresponds well with data published by Sabhapondit et al. There, decomposition of AMPS[®]/NNDMA copolymers is reported to start at $\sim 360^\circ\text{C}$.¹⁴ Consequently, thermal degradation of CaAMPS[®]-*co*-NNDMA can be excluded as the reason for its reduced FLA performance at 100°C . Instead, the results indicate that reduced fluid loss performance at high temperature is the consequence of reduced adsorption. Additional tests showed that in order to maintain an API fluid loss of ~ 40 mL at 100°C , a dosage as high as 0.8% bwoc of CaAMPS[®]-*co*-NNDMA is required.

When the MA modified terpolymer is used, the increase in API fluid loss occurring at high temperature is significantly less (from 38 mL/30 min at 27°C to 80 mL/30 min at 100°C ; see Figure 4). The reason is that the adsorbed amount of CaAMPS[®]-*co*-NNDMA-*co*-MA is less affected by temperature (4.7 mg/g at 27°C vs. 4.5 mg/g at 100°C). This result confirms that the MA-modified terpolymer exhibits a much improved performance with temperature. To explain this effect, the following considerations and experiments were made.

Through incorporation of only ~ 1.3 mol % of MA, the CaAMPS[®]-*co*-NNDMA-*co*-MA terpolymer backbone possesses segments holding additional car-

boxylate functionalities. In previous work relating to cement dispersants, $-\text{COO}^-$ groups have been found to be stronger anchor groups on cement surfaces than the sulfonate functionalities present in CaAMPS[®]-*co*-NNDMA.^{15,16} To confirm, we determined the specific anionic charge amounts of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, in alkaline solution (pH 12.6) in presence and absence of 0.6 g/L calcium ions using polyelectrolyte titration.

The results presented in Table V show that in a Ca^{2+} -loaded solution, incorporation of such minor quantity of MA into the copolymer has a surprisingly strong effect on the specific anionic charge amount. After addition of Ca^{2+} ions, the specific anionic charge amount of the terpolymer containing MA decreases by 31% versus only 4% for CaAMPS[®]-*co*-NNDMA. Apparently, the carboxylate functionalities of CaAMPS[®]-*co*-NNDMA-*co*-MA chelate calcium ions much stronger than the sulfonate groups contained in CaAMPS[®]-*co*-NNDMA. This way, it is confirmed that CaAMPS[®]-*co*-NNDMA-*co*-MA possesses a much stronger calcium binding capability than CaAMPS[®]-*co*-NNDMA. Consequently, the terpolymer exhibits a higher affinity to positively charged mineral surfaces, which causes the adsorbed amount of CaAMPS[®]-*co*-NNDMA-*co*-MA to be much less dependent of temperature. Through this mechanism, CaAMPS[®]-*co*-NNDMA-*co*-MA provides good fluid loss control of the cement slurry, even at high temperature.

Polymer adsorption was confirmed by zeta potential measurements. The neat cement slurry possesses a zeta potential of approximately -6 mV. When CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, were added at a dosage of 0.5% bwoc to the cement slurry, the zeta potentials decreased to values of -20 and -21 mV, respectively. The reason for this effect is the loading of negative charges onto the cement surface caused by adsorption of the polymers.

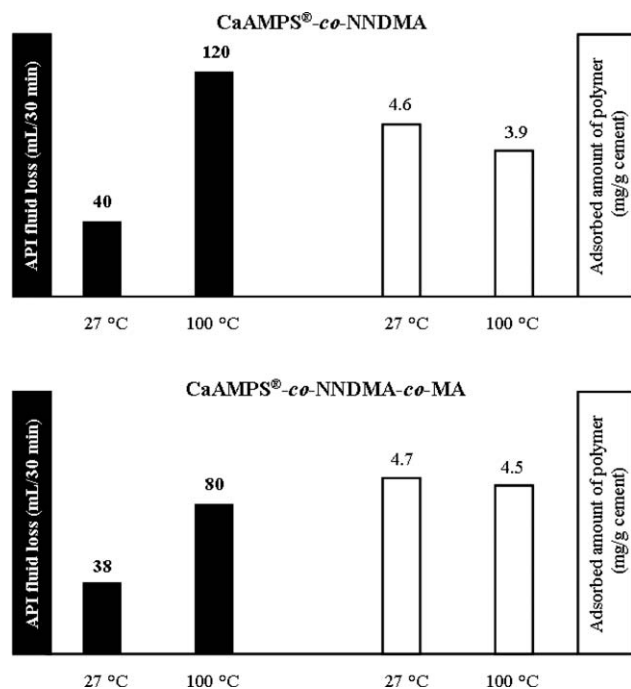


Figure 4 Relationship between API fluid loss (black bars) and adsorbed amount of fluid loss polymers (white bars), determined in cement slurries at 27 and 100°C , respectively (w/c ratio = 0.44; polymer concentration 0.5% by weight of cement).

Effect of temperature on sulfate concentration present in cement pore solution

To understand the reasons behind the reduced performance of CaAMPS[®]-*co*-NNDMA at high temperature even better, the concentrations of ions present in cement pore solution obtained at 27 and 100°C , respectively, were compared. Maitland et al. reported that calcium aluminate trisulfate (ettringite), an important cement hydrate phase, which is formed instantaneously on contact of cement with water, becomes unstable at temperatures $\geq 80^\circ\text{C}$ and decomposes into calcium monosulfaluminate (monosulfate) and gypsum.¹⁷ Consequently, we found that through this reaction, the sulfate

TABLE V
Specific Anionic Charge Amount of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, Measured in 0.1 M NaOH (pH 12.6) in Presence and Absence of 0.6 g/L Ca²⁺ (Polymer Concentration: 0.02 g/L)

Polymer	Specific anionic charge amount (C/g)		Reduction of anionic charge after Ca ²⁺ addition
	Water @ pH 12.6	Water @ pH 12.6 plus 0.6 g/L Ca ²⁺	
CaAMPS [®] - <i>co</i> -NNDMA	368	352	4 %
CaAMPS [®] - <i>co</i> -NNDMA- <i>co</i> -MA	402	275	31 %

concentration present in the cement pore solution collected at 100°C is higher than that measured at 27°C (8.3 g/L sulfate vs. 6.8 g/L sulfate). Opposite to this trend, the Ca²⁺ concentration remains nearly constant (0.7 g/L at 27°C vs. 0.6 g/L at 100°C).

Because of their high-anionic charge density, sulfate anions may also adsorb onto the surface of cement hydrates. Competition between sulfate and CaAMPS[®]-*co*-NNDMA for limited adsorption sites may occur. Therefore, it can be speculated that a higher sulfate concentration may also contribute to the reduced effectiveness of CaAMPS[®]-*co*-NNDMA at high temperature. To confirm this mechanism, adsorption of CaAMPS[®]-*co*-NNDMA and of sulfate on a mineral surface was compared.

Sulfate-dependent adsorption of FLA on silica

To quantify sulfate and FLA adsorption on positively charged mineral surfaces, we changed the adsorbent from reactive cement to inert silica flour. The reason is that API oil well cement always contains considerable amounts of sulfate (~ 3 to 4 wt % CaSO₄·*n*H₂O), which makes analysis of adsorbed amount of sulfate practically impossible. In highly alkaline suspensions (pH > 12), silica is negatively charged, which stems from deprotonated silanol groups present at the silica surface.¹⁸ We confirmed this for our silica flour sample by measurement of the zeta potential in 0.1M NaOH. At a water to silica ratio of 0.44, a value for the zeta potential of -7.7 mV was found. Addition of minor amounts of calcium ions (added as CaCl₂·2H₂O), however, causes a reversal in the sign of the surface charge to highly positive values (~ +12.8 mV at a dosage of 0.6 g/L Ca²⁺). The reason is adsorption of Ca²⁺ ions onto the negatively charged silica surface.¹⁹ This way, it is demonstrated that silica flour can provide positively charged adsorption sites for anionic FLA polymers in a similar way than cement.

Adsorption of sulfate and the FLAs on silica was determined at 100°C by using cement pore solutions collected at different temperatures. They differ in

their sulfate concentration, which is 6.8 g/L at 27°C and 8.3 g/L at 100°C. Independent of this fact, the adsorbed amount of CaAMPS[®]-*co*-NNDMA remains at 0.6 mg polymer/g silica only (see Figure 5). At the same time, a constant value of 0.1 mg of adsorbed sulfate/g silica was found. In spite of a temperature induced increase of the sulfate concentration present in the cement pore solution, the adsorption equilibrium does not shift toward higher sulfate and lower FLA adsorption. Obviously, competitive adsorption between this polymer and sulfate anions can be ruled out for the mechanism, which is behind the reduced effectiveness of this FLA polymer at high temperature. This instigates that

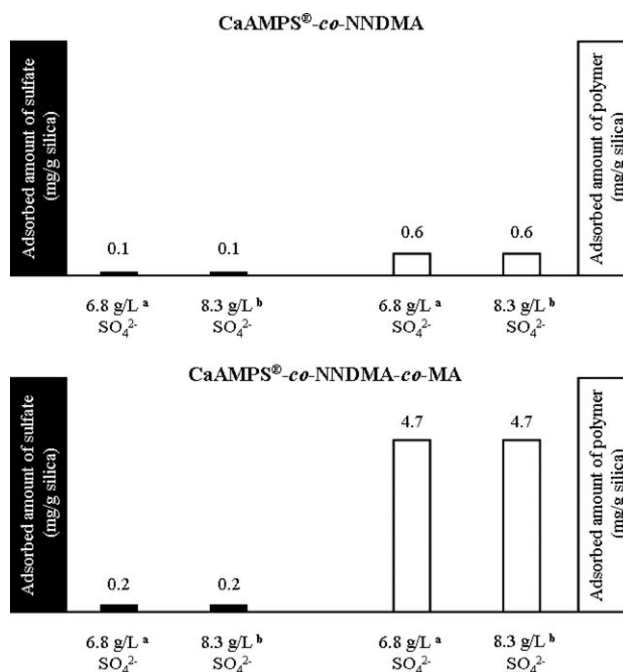


Figure 5 Adsorbed amounts of sulfate (black bars) and of fluid loss polymers (white bars) on silica as a function of sulfate concentration present in the mixing water, determined at 100°C (water/silica ratio = 0.44; polymer concentration 0.5% by weight of silica). (a) Cement pore solution collected at 27°C was used. (b) Cement pore solution collected at 100°C was used.

TABLE VI
Intrinsic Viscosity of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, Determined at Different Sulfate Concentrations Present in Cement Pore Solution and at 80°C (*w/c* Ratio = 0.44)

Polymer	Intrinsic viscosity (L/g)	
	6.8 g/L SO ₄ ²⁻ ^a	8.3 g/L SO ₄ ²⁻ ^b
CaAMPS [®] - <i>co</i> -NNDMA	0.36	0.33
CaAMPS [®] - <i>co</i> -NNDMA- <i>co</i> -MA	0.34	0.30

^a This test used cement pore solution collected at 27°C.

^b This test used cement pore solution collected at 100°C.

increased kinetic energy of the polymer molecules dissolved in water at 100°C decreases the adsorbed amount and is the reason for the reduced performance of CaAMPS[®]-*co*-NNDMA at high temperature.

The adsorbed amount of CaAMPS[®]-*co*-NNDMA-*co*-MA on silica also is independent of the sulfate concentration, but lies much higher at 4.7 mg polymer/g silica versus only 0.6 mg polymer/g silica for CaAMPS[®]-*co*-NNDMA. Owing to the incorporation of homopolymer blocks holding carboxylate anchor groups, this terpolymer exhibits a strong affinity to the positively charged silica surface, even at 100°C. Obviously, for this modified terpolymer and under these conditions, the Gibbs free energy of adsorption ΔG_{ads}^0 is higher than its kinetic energy. The result is improved performance of CaAMPS[®]-*co*-NNDMA-*co*-MA at high temperature.

Conformation of solvated FLA polymers

Another factor, which may influence the adsorption of AMPS[®]-based FLAs onto mineral surfaces, is the molecular conformation of the solvated polymer. For example, it has been demonstrated that sulfate ions present in cement pore solution cause shrinkage and coiling of polycarboxylate-type dispersants commonly used in concrete.²⁰ There, the consequence of this effect is lower adsorption and hence reduced dispersing power. To investigate the effect of sulfate ions on the conformation of solvated FLA polymers, we determined the intrinsic viscosity of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-

co-NNDMA-*co*-MA, respectively, dissolved in two different cement pore solutions at 80°C (the respective solvents were collected by filtration at 27 and 100°C, respectively). The results exhibited in Table VI demonstrate that for both polymers, a higher SO₄²⁻ concentration reduces the intrinsic viscosity (CaAMPS[®]-*co*-NNDMA: from 0.36 at 6.8 g/L sulfate to 0.33 L/g at 8.3 g/L sulfate; CaAMPS[®]-*co*-NNDMA-*co*-MA: from 0.34 L/g at 6.8 g/L sulfate to 0.30 L/g at 8.3 g/L sulfate). These data suggest that an elevated sulfate concentration causes some coiling of the solvated macromolecules.

To confirm this effect, the radius of gyration of these polymers was determined at increasing sulfate concentrations (see Table VII). It was found that for both polymers, $R_{g,z}$ decreases with increasing sulfate concentration. For example, $R_{g,z}$ of CaAMPS[®]-*co*-NNDMA exhibits a decrease from 64 nm in sulfate-free environment to 53 nm in the presence of 8.3 g/L SO₄²⁻. Similarly, the radius of gyration of CaAMPS[®]-*co*-NNDMA-*co*-MA decreases from 58 nm in the absence of sulfate to 41 nm at 8.3 g/L sulfate. Thus, it becomes evident that both macromolecules undergo similar shrinkage in the presence of sulfate.

Obviously, a coiled polymer will have to unfold to develop the maximum number of contact points per unit of surface area. Thus, an FLA polymer in coiled conformation will have lower tendency to adsorb than a stretched molecule, which exists in a sulfate-free solution.²¹ Additionally, a coiled polymer will generally exercise a reduced plugging effect compared to a fully stretched polymer, which can constrict the pores of the filter cake more effectively, simply because of its larger steric size. Consequently, the coiling effect observed instigates a slightly reduced performance for both FLA polymers.

CONCLUSIONS

Our study demonstrates that the performance of CaAMPS[®]-*co*-NNDMA, which presents a common FLA in oil well cementing, is negatively impacted by high temperature. The reason behind this effect is reduced adsorption, mainly caused by

TABLE VII
Radius of Gyration of CaAMPS[®]-*co*-NNDMA and CaAMPS[®]-*co*-NNDMA-*co*-MA, respectively, Determined at Different Sulfate Concentrations

Polymer	Radius of gyration (nm)		
	0 g/L SO ₄ ²⁻	6.8 g/L SO ₄ ²⁻ ^a	8.3 g/L SO ₄ ²⁻ ^b
CaAMPS [®] - <i>co</i> -NNDMA	64	62	53
CaAMPS [®] - <i>co</i> -NNDMA- <i>co</i> -MA	58	54	41

^a This sulfate concentration is present in cement pore solution collected at 27°C.

^b This sulfate concentration is present in cement pore solution collected at 100°C.

poor calcium binding capability of the sulfonate anchor groups, which coordinate with calcium atoms present on the mineral surface. At high temperature the kinetic energy of CaAMPS[®]-*co*-NNDMA increases to be equal to or exceed the Gibbs free energy of adsorption, ΔC_{ads}^0 , thus making adsorption less favorable. Shrinkage of the polymer owed to an increase in the sulfate concentration present in the cement pore solution, which in turn results from thermal degradation of ettringite, a cement hydrate mineral, which decomposes at temperatures $\geq 80^\circ\text{C}$, also contributes to this effect, whereas competitive adsorption between sulfate and the polymer does not significantly impact its adsorption behavior. This is in contrast to dispersant molecules based on polycarboxylate chemistry where numerous cases are documented describing a strong effect of sulfate on the adsorption of those admixtures.^{20,22}

Slightly modified CaAMPS[®]-*co*-NNDMA-*co*-MA possesses few homopolymer blocks holding vicinal carboxylate functionalities, which present much stronger anchor groups than sulfonates. The result is high and stable adsorption, independent of temperature and sulfate concentration. Consequently, its fluid loss performance is little affected by those two parameters. Obviously, the blocks of carboxylate functionalities are the key for the improved performance. This is evidenced through measurements of the calcium binding capability, which is significantly higher than that for CaAMPS[®]-*co*-NNDMA. It causes a stronger immobilization of the molecule on the mineral surface. Thus, CaAMPS[®]-*co*-NNDMA-*co*-MA is a more robust admixture, compared with its unmodified counterpart CaAMPS[®]-*co*-NNDMA. The benefit of incorporating a very minor amount of MA into another polymer (e.g., polypropylene) as a compatibilizer for a mineral surface (e.g., clay) has been described before.²³⁻²⁵ Our study demonstrates that this concept also applies to AMPS[®] copolymers and cementitious systems. In spite of this, performance of CaAMPS[®]-*co*-NNDMA-*co*-MA could be improved further by avoiding coiling of the macromolecule in the presence of sulfate. This may be accomplished, for example, by applying side chains onto the polymer backbone, which shield the polymer from the negative impact of increased ionic strength of the solvent.

The results of this study demonstrate that understanding the temperature-induced physicochemical processes involved in the interaction between these polymers and the mineral surfaces of cement and silica allows fine-tuning of the polymer structures to provide enhanced performance under specific condi-

tions. It is also demonstrated that a relatively minor modification of the polymer composition and structure can cause a surprisingly strong alteration of its properties. Finally, it provides insight into the variety of parameters, which can influence admixture behavior in a system as complex as hydrating cement.

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