

Impact of Temperature on the Solution Conformation and Performance of AMPS[®]- and AHPS-based Fluid Loss Polymers in Oil Well Cement

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A copolymer composed of 2-acrylamido-2-methyl propane sulfonic acid (AMPS[®]) and *N,N*-dimethylacrylamide (NNDMA) as well as a forpolymer based on AMPS[®], NNDMA, 1-allyloxy-2-hydroxy propane sulfonic acid (AHPS) and acrylic acid (AA) were synthesized and tested for their temperature stability. Both polymers were dissolved and aged in cement pore solution at temperatures between 100 and 220°C and 35 bar pressure, simulating conditions in actual well cementing. The influence of this high-temperature treatment on the fluid loss performance was assessed *via* high-pressure filtration tests. Water retention capacity and adsorption of AMPS[®]-*co*-NNDMA was found to decrease as a result of temperature-induced shrinkage of the stiff, linear polymer chain, as evidenced by dynamic light scattering (DLS) measurement of its hydrodynamic radius. Oppositely, the AHPS-based fluid loss additive did not exhibit coiling under high-temperature conditions. Therefore, its adsorption remained unaffected, and a stable fluid loss performance was observed.

Key words: AMPS[®], 1-Allyloxy-2-hydroxy Propane Sulfonic Acid (AHPS), Fluid Loss Additive, High-temperature Polymer, Oil Well Cement

Introduction

The sealing quality of cement determines the safety during the lifetime of deep oil and gas wells. In well completion, extraordinarily high pressures and temperatures which can reach 2000 bar and 260°C, respectively, as well as high salinity occurring in reservoir fluids present most challenging conditions. Such harsh conditions make it very difficult to control the properties of the cement slurry such as setting time, rheology, free water and fluid loss. For this reason, cementing is one of the most critical operations performed in the construction of a well bore [1, 2]. This became quite obvious from BP's Macando well blow-out in the U. S. Gulf of Mexico in 2010 which had its origin in a failed cement job across the gas reservoir [3, 4]. To ensure a cement seal which is impermeable to fluids and gases, various chemical additives are included into the slurry formulation [5].

One major group of admixtures are fluid loss additives (FLAs). These polymers prevent the uncontrolled migration of water from the cement slurry to the rock formation. This is achieved through formation of a tight filtercake which reduces the leak off rate. According to earlier work published by Desbrières [6, 7], anionic or non-ionic FLAs can reduce the filtercake permeability of cement slurries *via* three potential mechanisms: (1) through adsorption of large macromolecules on cement whereby the effective pore diameter in the filtercake is decreased; (2) through hydrated and swollen polymer particles (*e. g.* microgels) or polymer films which plug and constrict the pores in a filtercake; and (3) through modification of the filtercake structure by the FLA.

A broad variety of different fluid loss polymers is utilized by the oil industry. The largest group includes non-ionic or slightly negatively charged cellulose ethers such as hydroxyethyl cel-

lulose (HEC) or carboxymethyl hydroxyethyl cellulose (CMHEC) [8–10]. Recent studies demonstrated that the working mechanism of HEC relies on a dual effect, namely on intramolecular water sorption and the formation of hydrocolloidal-associated polymer networks [11]. CMHEC, on the other hand, shows a different and dosage-dependent behavior. At low dosages, adsorption of CMHEC molecules onto positively charged sites of the cement surface presents the predominant mode of action. However, when increasing the dosage above a certain threshold concentration (the “overlapping” concentration), associated polymer networks are formed which further improve fluid loss control [12]. Another example for a non-ionic FLA is unmodified or crosslinked polyvinyl alcohol (PVA) which reduces the filtercake permeability by forming a polymer film within the cement filtercake [13, 14]. Finally, cationic polymers were also found to decrease cement fluid loss. For instance, insoluble polyelectrolyte complexes obtained from the combination of positively charged polyethylene imine (PEI) and an anionic dispersant such as *e. g.* acetone-formaldehyde-sulfite effectively plug pores of the filtercake [15, 16].

To meet the industry’s growing demand for salt-tolerant, non-retarding FLAs, co- or terpolymers derived from acrylamide, *N*-vinylacetamide and/or 2-acrylamido-2-methyl propane sulfonic acid (AMPS[®]) were developed which perform well at elevated temperatures [17–20]. From this group, the most commonly used additive comprises a high molecular weight copolymer of AMPS[®] and *N,N*-dimethylacrylamide (NNDMA) which exhibits a considerable temperature stability (up to $\sim 150^\circ\text{C}$). It is stable against hydrolysis under the highly alkaline pH conditions of aqueous cement dispersions (pH ~ 13) as well as against salt contents up to 18% NaCl by weight of cement (bwoc) [20]. Recent work has shown that the water retention effect of AMPS[®]-NNDMA copolymers is achieved by polymer adsorption onto the cement surface [21]. A major drawback of this copolymer is its continuous loss of performance above 150°C . However, high-temperature wells such as the deepest offshore well ever planned near Hawaii island (4.000 m of water depth and 6.000 m of drilling depth below the Pacific Ocean sea floor) will encounter temperatures of up to 250°C [22]. To overcome this gap, recently a graft copolymer composed of humic acid, AMPS[®], NNDMA and acrylic acid exhibiting high ef-

fectiveness at and above 150°C was proposed [23]. However, so far the highest temperature stability (up to 200°C) was achieved with a forpolymer synthesized from AHPS, AMPS[®], NNDMA and acrylic acid utilizing *N,N*-methylenebisacrylamide (NNMBA) as crosslinking agent [24].

The aim of this work was to compare the effect of high temperature on the performance and molecular properties of two different AMPS[®]-based fluid loss polymers used in oil well cementing. For this purpose, a copolymer composed of AMPS[®] and NNDMA as well as a forpolymer containing AMPS[®], AHPS, NNDMA, and acrylic acid were synthesized, dissolved in cement pore solution and aged at temperatures between 100 and 220°C under 35 bar N_2 pressure. Afterwards, the performance of the heat-exposed polymer samples was tested utilizing static fluid loss experiments at room temperature. The performance data were correlated with the values on polymer adsorption assessed *via* the total organic carbon (TOC) method and zeta potential experiments. Additionally, the molecular properties and polymer radii (hydrodynamic radius, R_h , and radius of gyration, R_g) of the aged polymer samples were determined *via* anionic charge and gel permeation chromatography (GPC) measurements. Based on these results, an explanation for the different behaviors of the two polymers at high temperatures will be offered.

Experimental

Materials

Oil well cement

An API Class G oil well cement (“black label” from Dyckerhoff AG, Wiesbaden, Germany) corresponding to American Petroleum Institute (API) Specification 10A was used [25]. Its clinker composition was determined *via* quantitative powder X-ray diffraction (XRD) technique using a Rietveld refinement. The results are listed in Table 1. The amounts of gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) and hemi-hydrate ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) present in the cement sample were measured by thermogravimetry. Free lime (CaO) was quantified using the extraction method established by Franke [26]. According to the method developed by Blaine, the specific surface area of the cement sample was found to be $3058 \text{ cm}^2 \text{ g}^{-1}$ while its specific density was 3.18 kg L^{-1} , as measured by helium pycnometry. Particle size distribution of the cement sample was determined using a laser-based particle size analyzer which yielded a d_{50} value of $11 \mu\text{m}$ (see Table 1).

Table 1. Phase composition (Q-XRD, Rietveld), specific density, specific surface area (Blaine) and d_{50} value of an API Class G oil well cement sample.

C ₃ S	C ₂ S	C ₃ A _c	C ₄ AF	Free CaO	CaSO ₄ ·2 H ₂ O	CaSO ₄ ·0.5 H ₂ O	CaSO ₄	Specific density (kg L ⁻¹)	Specific surface area (cm ² g ⁻¹)	d_{50} value (μm)
(wt-%)	(wt-%)	(wt-%)	(wt-%)	(wt-%)	(wt-%)	(wt-%)	(wt-%)			
59.6	22.8	1.2	13.0	< 0.3	2.7 ^a	0.0 ^a	0.7	3.18	3,058	11

^a Measured by thermogravimetry; C₃S: tricalcium silicate (Ca₃(SiO₄)O); C₂S: dicalcium silicate (Ca₂SiO₄); C₃A_c: cubic modification of tricalcium aluminate (Ca₉Al₆O₁₈); C₄AF: tetracalcium aluminate ferrite (Ca₄Al₂Fe₂O₁₀).

AMPS[®]-co-NNDMA fluid loss additive

The copolymer of 2-acrylamido-2-methyl propane sulfonic acid and *N,N*-dimethylacrylamide (molar ratio of monomers = 1 : 0.63) was synthesized using aqueous free radical copolymerization as described in a previous work [21]. Laboratory-grade AMPS[®] (Type 2404, Lubrizol, Wickliffe, OH, USA; AMPS[®] is a registered trademark of the Lubrizol company) and NNDMA (Sigma-Aldrich Chemical, Munich, Germany) were used as received. The chemical structure of AMPS[®]-co-NNDMA is shown in Fig. 1. GPC analysis of the FLA produced molecular weights of 790 000 g mol⁻¹ (M_w) and 470 000 g mol⁻¹ (M_n) at a PDI of 1.7. The GPC spectrum and further data on the polymer can be found in the literature [21].

AMPS[®]-co-NNDMA-co-AHPS-co-AA fluid loss additive

The forpolymer of 2-acrylamido-2-methylpropane sulfonic acid (AMPS[®]), *N,N*-dimethylacrylamide (NNDMA), allyloxy-2-hydroxy propane sulfonic acid (AHPS), and acrylic acid (AA) was synthesized *via* aqueous free-radical copolymerization according to a method described in a previous article [24]. Laboratory-grade AMPS[®] (Type 2404, Lubrizol, Wickliffe, OH, USA), NNDMA (Sigma-Aldrich Chemical, Munich, Germany), AHPS (BIMAX, Glen Rock, PA, USA), and AA (Merck KGaA, Darmstadt, Germany) were used as received. The chemical structure of the FLA containing the AHPS building block is shown in Fig. 1. GPC analysis of the fluid loss additive produced molecular weights of 200 000 g mol⁻¹ (M_w) and 90 000 g mol⁻¹ (M_n)

at a PDI of 2.2. The GPC spectrum of the polymer and further data can be found in the literature [24].

Instruments and procedures

Cement characterization

Phase composition of the cement sample was obtained *via* powder X-ray diffraction using a Bruker axS D8 Advance instrument (Karlsruhe, Germany) with Bragg-Bretano geometry. The TOPAS 3.0 software was used to quantify the amounts of the individual phases of the sample following Rietveld's method of refinement [27]. The instrument was equipped with a scintillation detector using CuK_α ($\lambda = 1.5406 \text{ \AA}$) radiation with a scanning range between 5° and 80° (2θ). The specific density of the cement sample was measured with an Ultrapycnometer[®] 1000 (Quantachrome Instruments, Boynton Beach, FL, USA). The specific surface area of the sample was determined utilizing a Blaine instrument (Toni Technik, Berlin, Germany). The average particle size (d_{50} value) was obtained on a laser-based particle size analyzer (1064 instrument from Cilas, Marseille, France).

Temperature exposure of polymers

Thermal ageing of the FLAs was conducted in an OF-ITE roller oven (OFI Testing Equipment Inc., Houston, TX, USA). For this purpose, 20 g of AMPS[®]-co-NNDMA or of the AHPS-modified forpolymer was dissolved in 230 g of cement pore solution (resulting polymer concentration: 8 wt-%) and poured into a 500 mL Teflon liner which was transferred into a stainless-steel grade ageing cell (#175-50 Stainless Steel Grade 316, 500 mL, OFI Testing Equipment Inc.,

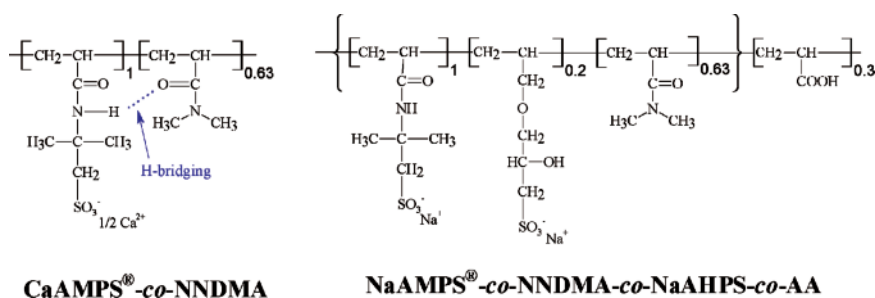


Fig. 1. Chemical structures of CaAMPS[®]-co-NNDMA and NaAMPS[®]-co-NNDMA-co-NaAHPS-co-AA.

Houston, TX, USA) and sealed. An N_2 pressure of 35 bar was applied to the cell which was rotated at 25 rpm in the roller oven. The sample was then heated to the desired temperature (100, 120, 140, 160, 180, 200, and 220°C) and left rotating for 8 h. Thereafter, the cells were removed from the oven, first cooled on air and then in a water bath to room temperature before further analysis was performed.

Cement slurry preparation

Cement slurries were prepared in accordance with the procedures described in “Recommended Practice for Testing Well Cements”, API Recommended Practice 10B, issued by the American Petroleum Institute [28]. The slurries were mixed at a water-to-cement (w/c) ratio of 0.44 using a blade-type laboratory blender obtained from Waring Products Inc. (Torrington, CT, USA). Admixture dosages are generally stated in % by weight of cement (bwoc). For slurry preparation, the aged solutions of the fluid loss additives (the samples were neither purified nor dried after thermal treatment) were mixed with deionized (DI) water, and this combine was used as mixing water. Then, within 15 s, the cement was added to the mixing water placed in the 1000 mL cup of the Waring blender and mixed for 35 s at 12,000 rpm. To ensure homogeneous consistency, all slurries were stirred for 20 min at 27°C in an atmospheric consistometer (model 1250 from Chandler Engineering, Tulsa, OK, USA). The pore solution of the neat cement slurry (no polymer present) was collected by vacuum filtration (12 mbar) from this cement slurry using a diaphragm vacuum pump (Vacuubrand GmbH, Wertheim, Germany). Typically, ~ 150 mL of pore solution were obtained from a slurry prepared from 700 g of cement and 308 mL of DI water.

API static fluid loss

The static fluid loss was measured at 27°C using a 500 mL high-temperature, high-pressure (HTHP) stainless-steel filter press cell manufactured by OFI Testing Equipment Inc. (Houston, TX, USA). The design of this HTHP filter cell and its operation are described in detail in a norm issued by the American Petroleum Institute (API) [28]. After pouring the homogenized slurry obtained from the atmospheric consistometer into the HTHP cell, a heating jacket (OFI Testing Equipment Inc., Houston, TX, USA) was used to adjust the test temperature. Then, a differential pressure of 70 bar N_2 was applied at the top of the cell. Filtration proceeded through a 22.6 cm² (3.5 in²) mesh metal sieve placed at the bottom of the cell. The filtrate volume collected within 30 min was doubled as described by API RP 10B and regarded as API fluid loss of the corresponding slurry [28]. The maximum deviation of the fluid loss value was ± 5 mL per 30 min.

Polymer characterization

Solid contents of the aqueous polymer solutions were determined using an infrared drying balance (MA35 from Sartorius AG, Göttingen, Germany). Drying conditions were 15 min at 90°C. The values presented are the averages obtained from three separate measurements.

For assessment of molecular properties, size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn, Germany, equipped with a RI detector 2414, Waters, Eschborn, Germany) and an 18 angle dynamic light scattering detector (Dawn EOS from Wyatt Technologies, Santa Barbara, CA, USA) were used. The AMPS[®]-NNDMA copolymer was 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 polymer radii ($R_{h(z)}$ and $R_{g(z)}$) were determined using 0.2 M aqueous $NaNO_3$ solution (adjusted to pH = 9.0 with NaOH) as eluent at a flow rate of 1.0 mL min⁻¹. Because of the lower molecular weight and the detection limits of the columns, the AMPS[®]-NNDMA-AHPS-AA for-polymer was separated on another GPC instrument. There, an Ultrahydrogel[™] precolumn and three Ultrahydrogel[™] columns (120, 250 and 500; Waters, Eschborn, Germany) using a 0.1 M aqueous $NaNO_3$ solution (adjusted to pH = 12.0 with NaOH) as an eluent at a flow rate of 1.0 mL min⁻¹ were utilized. The value of dn/dc used to calculate M_w and M_n for all polymers was 0.156 mL g⁻¹ (value for polyacrylamide) [29]. The temperature-exposed polymers were measured as obtained after ageing, *i. e.* no purification step was performed.

Specific anionic charge amounts of the polymers were determined in cement pore solution using a PCD 03 pH apparatus (BTG Müttek GmbH, Herrsching, Germany). Charge titration was carried out according to a literature procedure employing a 0.001 N solution of laboratory grade poly(diallyldimethylammoniumchloride) from BTG Müttek GmbH, Herrsching, Germany, as cationic polyelectrolyte [30]. The values presented in this study are the averages obtained from three independent measurements. The deviation for this method was found to be ± 5 C g⁻¹.

Retained amounts

The amounts of polymers retained on cement were determined from the filtrates collected by vacuum filtration of the cement slurries. A High TOC II apparatus (Elementar, Hanau, Germany) equipped with a CO₂ and NO_x detector was used to quantify the polymer concentrations *via* total organic carbon (TOC) content. Before conducting the TOC analysis, the alkaline cement filtrate containing the portion of non-adsorbed polymer was adjusted to pH = 7.0 by adding 0.01 M H₃PO₄. From the difference of the polymer concentrations in the initial solution (no cement present) and after

contact with cement, the amount of polymer retained was calculated.

Zeta potential measurements

The zeta potential of the cement slurries was measured at room temperature with an electro acoustic spectrometer (DT-1200 from Dispersion Technology Inc., Bedford Hills, NY, USA) [31]. Because the zeta potentials were determined as a function of time (here 30 min), the cement slurries were poured immediately after mixing into the cup of the spectrometer and measured without homogenization in the atmospheric consistometer. The accuracy of this method was ± 0.5 mV.

Results and Discussion

High-temperature fluid loss performance of AMPS[®]-co-NNDMA

To study the potential effect of high temperatures on the effectiveness of the CaAMPS[®]-co-NNDMA fluid loss additive, solutions of the polymer in cement pore solution (polymer concentration 8 wt.-%) were heated to temperatures between 100 to 220°C for 8 hours. Afterwards, static fluid loss tests were conducted at room temperature. Room temperature was chosen in order to eliminate the effects of different cement hydrates formed at increasing temperatures which can significantly affect cement-additive interaction and filtercake porosity and thus make comparisons at different temperatures impossible. Furthermore, fluid loss tests $\geq 100^\circ\text{C}$ would necessitate the incorporation of retarders into the cement slurry which can strongly impact the performance of other additives including FLAs [24, 32, 33]. After ageing, all samples holding the AMPS[®]-NNDMA copolymer showed a colorless precipitate which *via* XRD and elemental analysis was identified as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and did not contain any organic polymer.

Fig. 2 displays the fluid loss values of API Class G cement slurries (w/c ratio = 0.44) containing 0.5% bwoc of CaAMPS[®]-co-NNDMA aged at different temperatures. At ageing temperatures between 100 and 120°C the fluid loss remains constant at a filtrate volume of ~ 33 mL. Beginning at 140°C, however, API fluid loss increases. A further rise in temperature accelerates this trend. Thus, after exposure to 220°C a fluid loss volume of 72 mL was observed which presents a 118% increase, compared to the initial fil-

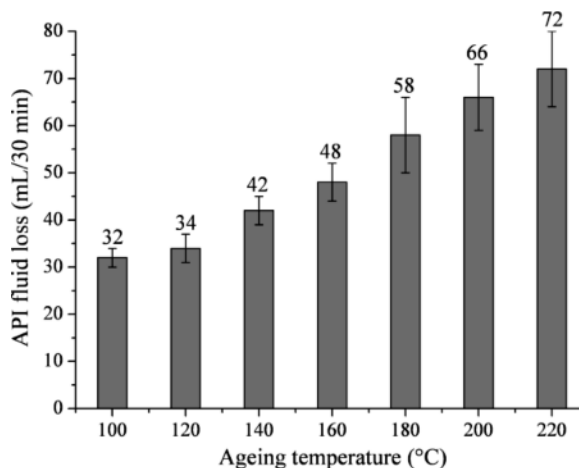


Fig. 2. API fluid loss values of API Class G cement slurries (w/c = 0.44) containing 0.5% bwoc CaAMPS[®]-co-NNDMA aged at temperatures between 100 and 220°C, measured at room temperature.

trate value. These data demonstrate that high temperatures have a significant effect on the fluid loss performance of the CaAMPS[®]-NNDMA copolymer.

It has been reported that the working mechanism of CaAMPS[®]-co-NNDMA is based on adsorption onto the surfaces of hydrating cement particles, whereby the permeability of the filtercake is reduced [21]. A potential reason for the loss in fluid loss performance would be a temperature-induced alteration of the polymer conformation (*e. g.* coiling or chemical degradation) which results in decreased adsorption. In order to probe into this hypothesis, the amounts of polymer retained in the filtercake were measured applying the TOC method. The results are displayed in Fig. 3. It becomes obvious that at ageing temperatures of 100 and 120°C, the retained amounts of the FLA remain constant at 4.0 mg g^{-1} cement. However, beginning at 140°C and following the trend in the fluid loss experiments the retained amounts start to decline and drop to 3.4 mg g^{-1} cement at 220°C. These data suggest that polymer adsorption is indeed affected by high-temperature exposure of the polymer.

To confirm this effect, zeta potential measurements were performed on cement slurries holding 0.5% bwoc of CaAMPS[®]-co-NNDMA aged at rising temperatures. The data obtained are presented in Fig. 4. Adsorption of the anionic FLA on cement instigates a highly negative surface potential, as evidenced there. Again, the cement slurries holding the FLA aged at

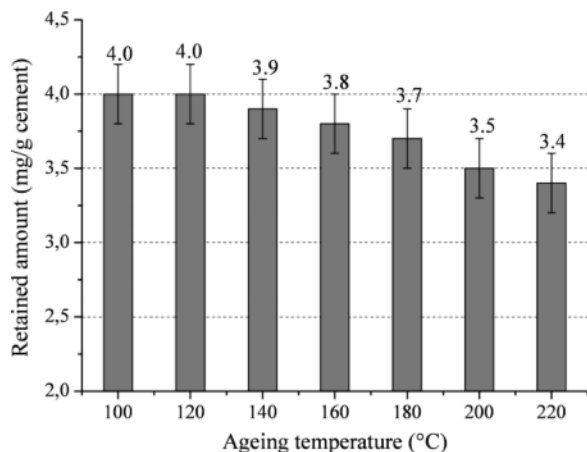


Fig. 3. Retained amounts of CaAMPS[®]-*co*-NNDMA in cement slurries ($w/c = 0.44$) containing 0.5% bwoc FLA aged at temperatures between 100 and 220 °C, measured at room temperature.

100 and 120 °C show a constant zeta potential value of ~ -18.5 mV. However, at ≥ 140 °C an increase in exposure temperature leads to less negative zeta potential values, *e. g.* -17.9 mV at 140 °C or -16.1 mV at 220 °C. The data clearly confirm that beginning at 140 °C, adsorption of this polymer on cement is significantly decreased which explains its reduced fluid loss performance. The reason behind the lower adsorption was identified later.

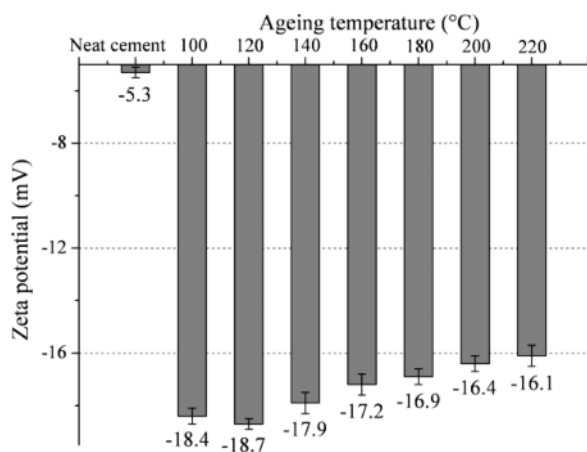


Fig. 4. Zeta potential of API Class G oil well cement slurries ($w/c = 0.44$) holding 0.5% bwoc of CaAMPS[®]-*co*-NNDMA fluid loss additive aged at temperatures between 100 and 220 °C, measured at room temperature.

High-temperature fluid loss performance of the AHPS forpolymer

Next, the influence of heat treatment on the fluid loss performance of NaAMPS[®]-*co*-NNDMA-*co*-NaAHPS-*co*-AA was studied. Different to the AMPS[®] copolymer which always produced turbid solutions after ageing, samples of the AHPS-based FLA when removed from the oven were completely clear, although the color of the polymer solutions had changed from yellowish to slightly brown. This difference can be explained as follows: AMPS[®]-*co*-NNDMA was synthesized as a calcium salt, while the AHPS FLA was prepared as sodium salt. The Ca^{2+} present in AMPS[®]-*co*-NNDMA reacts with sulfate from the cement pore solution to form gypsum which then precipitates as a colorless solid. Oppositely, the AHPS FLA forms sodium sulfate which exhibits very good solubility and does not precipitate.

Using these polymers, static filtration tests were carried out at room temperature. Again, a polymer dosage of 0.5% bwoc was chosen. The results are displayed in Fig. 5. Here, API fluid loss of the polymer samples aged at temperatures between 100 and 180 °C remained constant (values around 62–66 mL). Surprisingly, at 200 °C even an improvement in fluid loss performance was observed for this polymer. To probe into this, an additional experiment with a decreased FLA dosage of 0.4% bwoc (FLA aged at 200 °C) was performed under

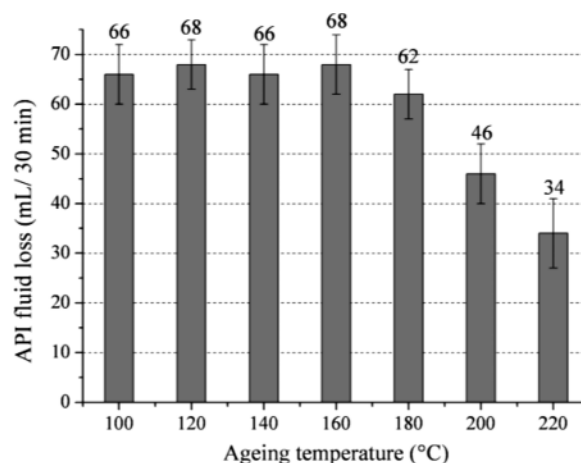


Fig. 5. API fluid loss values of API Class G cement slurries ($w/c = 0.44$) containing 0.5% bwoc of AHPS-based FLA aged at temperatures between 100 and 220 °C, measured at room temperature.

Table 2. Retained amounts of polymer and zeta potentials of cement slurries ($w/c = 0.44$) containing 0.5% bwoc AHPS-based fluid loss additive which was exposed for 8 h to temperatures between 100 and 220 °C.

Ageing temperature (°C)	Retained amount (mg g^{-1} cement)	Zeta potential (mV)
100	2.7(± 0.1)	-17.2(± 0.2)
120	2.7(± 0.2)	-16.8(± 0.3)
140	2.6(± 0.2)	-17.1(± 0.2)
160	2.7(± 0.1)	-17.1(± 0.1)
180	2.8(± 0.2)	-17.1(± 0.2)
200	3.5(± 0.2)	-18.0(± 0.3)
220	3.7(± 0.2)	-17.9(± 0.4)

identical conditions. There, an API fluid loss value of 64 mL was achieved which is comparable to that obtained with 0.5% bwoc of FLA aged at 180°C or less. This result demonstrates that the performance of the AHPS FLA does not decrease, but instead improves. A further increase of the ageing temperature to 220°C causes even lower fluid loss values (34 mL). This effect, however, is owed to beginning instability and disintegration of the cement suspension at this temperature. Here, sedimentation of the fine cement particles which plug the pores of the filtercake leading to a so called “faked fluid loss” was observed.

Similar to the AMPS[®]-NNDMA copolymer, adsorption of the AHPS forpolymer on cement was checked *via* TOC measurement. The results are displayed in Table 2. Between ageing temperatures of 100 to 180°C, the retained amounts of the AHPS-based fluid loss polymer were found constant at a value of $\sim 2.7 \text{ mg g}^{-1}$ cement, while 200°C storage led to a significant increase in the retained amount to 3.5 mg g^{-1} cement. Again, this increase signifies an improvement in the performance of the AHPS forpolymer.

To confirm this trend, zeta potential measurements of cement slurries holding 0.5% bwoc of AHPS polymer were carried out (see Table 2). It was found that the surface charge of the cement particles remained constant at values around -17.0 mV , independent of the ageing temperatures which were between 100 and 180°C. At an ageing temperature of 200°C, however, the zeta potential value increased to -18.0 mV , thus proving increased adsorption of the polymer and explaining its improved fluid loss performance.

The data presented here suggest that adsorption of the AHPS-based polymer is not negatively affected by exposure to high temperatures. It explains the superior performance over the CaAMPS[®]-*co*-NNDMA fluid loss additive at high temperatures.

Effect of high temperatures on the molecular properties of AMPS[®]-co-NNDMA

To clarify the reason behind the reduced adsorption and resulting decrease in fluid loss performance of heat-treated AMPS[®]-*co*-NNDMA, its temperature-dependent molecular properties were determined *via* anionic charge titration and GPC measurements. The results are listed in Table 3. In adsorption, the anionic sulfonate groups present the anchor groups for the copolymer which interact with positively charged sites existing on the surfaces of the cement particles. Thus, a decrease in anionic charge of the polymer as a consequence of thermal treatment presents a potential reason for reduced adsorption. However, the titration experiments produced values for the anionic charge of $\sim -400 \text{ C g}^{-1}$ for all samples. Therefore, a decrease in anionic charge (*e. g.* from oxidation of the sulfonate groups to sulfate) can be excluded as a reason for the

Table 3. Molar masses (M_w , M_n), polydispersity index (PDI), hydrodynamic radius ($R_{h(z)}$), radius of gyration ($R_{g(z)}$), Burchard parameter and anionic charge amount in cement pore solution (CPS) for an AMPS[®]-*co*-NNDMA fluid loss additive after 8 h of exposure to temperatures between 100 and 220 °C.

Ageing temperature (°C)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	$R_{g(z)}$ (nm)	$R_{h(z)}$ (nm)	Burchard parameter $R_{g(z)}/R_{h(z)}$	Anionic charge amount in CPS (C g^{-1})
100	638 600	919 600	1.4	52.1	20.0	2.6	-406
120	587 100	874 900	1.5	54.8	19.7	2.8	-429
140	598 700	857 400	1.4	44.3	20.0	2.2	-426
160	606 000	840 300	1.4	37.1	19.5	1.9	-411
180	651 200	868 600	1.3	34.6	18.8	1.8	-402
200	384 400	588 100	1.5	26.6	18.0	1.5	-398
220	330 300	516 300	1.6	20.8	21.6	1.0	-412

loss in fluid loss performance of the AMPS[®]-NNDMA copolymer.

Next, the possibility of temperature-induced polymer fragmentation and hydrolysis of the amide group present in the AMPS[®] monomer was checked *via* UV/Vis and NMR spectroscopy and GPC measurements. Both UV/Vis and NMR spectroscopy (spectra not shown here) revealed that no changes in the polymer samples had occurred after ageing at high temperatures, thus indicating that no fragmentation has taken place after heat exposure. Furthermore, GPC measurements produced similar results with respect to M_w , M_n and PDI (see Table 3). At ageing temperatures of 100 to 180°C, the molecular weights of the polymer samples were found to remain constant at $\sim 870\,000$ Da (M_w) and $\sim 600\,000$ Da (M_n), respectively. At ageing temperatures of 200 and 220°C, however, the polymer chain starts to undergo fragmentation, resulting in significantly decreased molecular weights of $\sim 520\,000$ Da (M_w) and $\sim 330\,000$ Da (M_n), respectively. However, the decline in adsorption and performance of the polymer already starts at 140°C, as reported before. Thus, polymer fragmentation was excluded as a reason behind the decreased fluid loss performance of AMPS[®]-*co*-NNDMA at $\geq 140^\circ\text{C}$.

Finally, alteration of the solution conformation of the polymer, *e. g.* from stretched to coiled, was considered as the reason for reduced adsorption and performance. This was probed *via* determination of the polymer radii ($R_{g(z)}$ and $R_{h(z)}$) of the heat-treated polymer samples (see Table 3). There, the hydrodynamic radius ($R_{h(z)}$) was found to be unaffected by the rising temperature and stayed constant at values between 18 to 20 nm. However, the radius of gyration ($R_{g(z)}$) shows quite a different behavior. At ageing temperatures of 100 and 120°C, $R_{g(z)}$ remains constant at values of

~ 53 nm. Beginning at 140°C, it decreases steadily until it reaches 20.8 nm at 220°C. This value is less than half of the radius at 100°C. The data demonstrate that at temperatures above 120°C, this polymer begins to coil. The coiling phenomenon was further confirmed by calculation of the so-called Burchard parameter which is obtained from the quotient of $R_{g(z)}$ to $R_{h(z)}$ (see Table 3) [34]. At ageing temperatures of 100 and 120°C, the Burchard parameter shows a constant value of ~ 2.7 which corresponds to the conformation of a stiff polymer chain. When the temperature is increased further, the value for the Burchard parameter decreases significantly and reaches a value of 1.0 at 220°C which represents the solution conformation of a tight statistic coil. Interestingly, it has been reported before that sulfate ions can have a similar coiling effect on AMPS[®]-based fluid loss additives [35]. Increased sulfate concentrations present in cement can induce polymer shrinkage which leads to decreased adsorption. Apparently, high temperatures can affect the AMPS[®]-*co*-NNDMA polymer in a similar way.

Effect of high temperatures on the molecular properties of AHPS FLA

In order to explain the superior performance of the AHPS-based fluid loss additive compared to CaAMPS[®]-*co*-NNDMA, its molecular properties after thermal treatment were determined. Table 4 exhibits the values for the anionic charge amounts of the polymer samples after ageing. Up to 220°C the anionic charge remains constant at ~ -485 C g⁻¹. This value is significantly higher than that for AMPS[®]-*co*-NNDMA (~ -400 C g⁻¹).

Furthermore, the molecular weights of the aged polymer samples were determined *via* GPC measure-

Table 4. Molar masses (M_w , M_n), polydispersity index (PDI), hydrodynamic radius ($R_{h(z)}$), radius of gyration ($R_{g(z)}$), Burchard parameter and anionic charge amount in cement pore solution (CPS) for an AHPS-based fluid loss additive after 8 h of exposure to temperatures between 100 and 220°C.

Ageing temperature (°C)	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI	$R_{g(z)}$ (nm)	$R_{h(z)}$ (nm)	Burchard parameter $R_{g(z)}/R_{h(z)}$	Anionic charge amount in CPS (C g ⁻¹)
100	94 500	202 700	2.1	23.8	15.1	1.6	-489
120	88 300	196 500	2.2	24.0	15.0	1.6	-488
140	88 000	191 100	2.2	22.8	14.0	1.6	-482
160	88 200	190 300	2.2	23.6	14.7	1.6	-486
180	88 600	185 200	2.1	23.1	14.5	1.6	-490
200	86 700	177 200	2.0	23.2	14.0	1.7	-447
220	70 100	179 100	2.6	25.0	17.6	1.5	-467

ment (see Table 4). They were found to be constant at $\sim 190\,000$ Da (M_w) and $\sim 90\,000$ Da (M_n), respectively. No fragmentation owing to thermal treatment was detected. The molecular weights measured for the AHPS-based FLA are significantly lower compared to those for AMPS[®]-*co*-NNDMA which exhibits an M_w of $\sim 870\,000$ Da and an M_n of $\sim 600\,000$ Da.

Next, potential changes in the solution conformation of the AHPS-based FLA were investigated *via* determination of the molecular radii. Table 4 exhibits the hydrodynamic radius ($R_{h(z)}$), the radius of gyration ($R_{g(z)}$) and the Burchard parameter of the heat-treated polymer samples. Interestingly, for this polymer the hydrodynamic radius $R_{h(z)}$ as well as the radius of gyration $R_{g(z)}$ are not affected by high temperatures and remain constant at values of $\sim 14\text{--}17$ nm ($R_{h(z)}$) and $\sim 23\text{--}25$ nm ($R_{g(z)}$). Upon thermal exposure, this polymer does not undergo shrinkage and coiling which differentiates it significantly from the AMPS[®]-NNDMA copolymer. Because of its stable conformation, fluid loss performance of this polymer is not affected at high temperatures. This observation is supported by the Burchard parameter which independent of the ageing temperature lies at 1.6 for all polymer samples (Table 4). Such a value for the Burchard parameter represents a linear statistic coil which is not optimal to achieve high polymer adsorption. However, this deficiency is compensated by the forpolymer's higher anionic charge which generally promotes polymer adsorption.

To explain the different conformational stabilities of AMPS[®]-*co*-NNDMA and the AHPS-based forpolymer, we propose the model as follows: In the AMPS[®]-NNDMA copolymer, hydrogen bonds can develop between the amide hydrogen atom of AMPS[®] and the carbonyl functionality of NNDMA (see Fig. 1). This interaction causes the conformation of the unaged AMPS[®]-*co*-NNDMA to be that of a stiff linear chain. During heat treatment, these hydrogen bonds are disrupted as a result of increased rotation owing to higher thermal energy. Consequently, the polymer chain now can coil. In the AHPS forpolymer, however, incorporation of the AHPS monomer at large prevents formation of such hydrogen bonds between AMPS[®] and NNDMA. Therefore, this polymer exhibits a more coiled conformation from the beginning, and high temperature does not affect its performance as fluid loss additive.

Conclusion

The fluid loss performances of AMPS[®]-*co*-NNDMA and AMPS[®]-*co*-AHPS-*co*-NNDMA-*co*-AA fluid loss additives in cement were compared after heat treatment in cement pore solutions at temperatures between 100 and 220°C. The performance of the AMPS[®]-NNDMA copolymer was found to decrease significantly as a result of thermal exposure. However, no fragmentation of the polymer chains or precipitation from solution was observed. Instead, measurements of the polymer radii revealed that shrinkage and coiling of the polymer chain occur at temperatures $\geq 140^\circ\text{C}$ which lead to reduced adsorption. In contrast to this, fluid loss performance of the AHPS-based forpolymer was not affected by high temperatures. This polymer does neither fragment nor precipitate and retains its solution conformation of a linear statistic coil even after thermal exposure, thus no change in its adsorption behavior on cement was observed.

The data presented in this study demonstrate that in high-temperature applications, polymers which possess a stable solution conformation in cement pore solutions are more advantageous. While polymers which rely on a large and stretched trunk chain such as present in AMPS[®]-*co*-NNDMA to produce excellent fluid loss fail at higher temperatures when the stretched chains shrink. Therefore, when designing cement fluid loss additives for high-temperature wells, apart from polymer degradation the possibility of temperature-induced changes in the polymer's solution conformation needs to be tested and taken into account. One potential strategy to achieve polymers which will not shrink at elevated temperatures is the synthesis of rather coiled polymers which at the same time possess a high anionic charge, similar to the AHPS-based FLA studied here. The disadvantage of this strategy is a higher dosage required at lower temperatures.

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