

Synthesis, Effectiveness, and Working Mechanism of Humic Acid- $\{$ Sodium 2-acrylamido-2-methylpropane sulfonate-*co*-*N,N*-dimethyl acrylamide-*co*-acrylic acid $\}$ Graft Copolymer as High-Temperature Fluid Loss Additive in Oil Well Cementing

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ABSTRACT: Monomers of 2-acrylamido-2-methylpropane sulfonic acid (AMPS[®]), *N,N*-dimethyl acrylamide (NNDMA) and acrylic acid (AA) were grafted on humic acid as backbone by aqueous free radical copolymerization in such a manner that a graft copolymer possessing lateral terpolymer chains was obtained. Molar ratios between AMPS[®], NNDMA, and AA were found to be 1 : 1.54 : 0.02 and the ratio between backbone and graft chain was 20 : 80 wt %. The synthesized fluid loss additive (FLA) was characterized by size exclusion chromatography (SEC), charge titration, and Brookfield viscometry. Thermogravimetric and SEC analysis revealed stretched backbone worm architecture for the polymer whereby humic acid constitutes the backbone decorated with lateral graft chains. Grafting was confirmed by SEC data (R_g) and by ineffectiveness of a blend of AMPS[®]-NNDMA-AA copolymer with humic acid. Their performance as high temperature FLA was studied at 150°C by measuring static

filtration properties of oil well cement slurries containing 35% bwoc of silica fume and 1.2% bwoc AMPS[®]-*co*-itaconic acid retarder. At this temperature, 1.0% bwoc graft copolymer achieves API fluid loss value of 40 mL, thus confirming high effectiveness. The graft copolymer viscosifies cement slurries less than other common synthetic FLAs. The working mechanism of the graft copolymer was found to rely on adsorption onto surface of hydrating cement, as was evidenced by adsorption and zeta potential measurements. Adsorption is hardly affected by temperature and results in constriction of the filter cake pores. The study provides insight into performance of cement additives under the harsh conditions of high temperature and high pressure. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: oil well cement; graft copolymer; humic acid; high temperature; fluid loss additive

INTRODUCTION

In oil well cementing, water-soluble polymers known as fluid loss additives are applied to provide water retention to cement slurries. They perform at demanding conditions occurring in well bores such as high temperature, pressure, and salinity.^{1,2} Deep oil or gas wells are characterized by high bottom hole temperatures which may range up to 260°C (500°F). The principal function of filtration control additives is to control the loss of water from the cement slurry to porous formations, thereby preventing rapid dehydration and loss of pumpability of the cement slurry.³

Currently, a variety of different polymers is employed for the purpose of fluid loss control. At

low temperatures (up to 100°C), unmodified or crosslinked polyvinyl alcohol (PVA) is used. Its working mechanism is based on film formation within the cement filter cake.^{4,5} While in the medium temperature range (50–150°C) cellulose ethers, namely hydroxyethyl cellulose (HEC), and carboxymethyl hydroxyethyl cellulose (CMHEC) are prevalent.^{6–8} Their effectiveness relies on the formation of large colloidal polymer associates once a specific “overlapping” concentration is transgressed (HEC), and on adsorption onto cement (CMHEC).⁹ Additionally, polyethylene imine (PEI) has been applied for the same purpose, but was dropped by the industry in recent years because of its toxicity to fishes and other aquatic species. Interestingly, PEI achieves fluid loss control by forming large polyelectrolyte complexes with anionic dispersants such as acetone-formaldehyde-sulfite polycondensate.¹⁰ For high temperature high pressure fluid loss control, synthetic sulfonated copolymers have become common. Among them are copolymers based on 2-acrylamido methane propane sulfonic acid (AMPS[®]),

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TABLE I
Phase Composition (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 ·0.5 H ₂ O (wt %)	CaSO ₄ (wt %)	Specific density (kg/L)	Specific surface area (cm ² /g)	d_{50} value (μ m)
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 (Ca₃Al₆O₁₈); C₄AF, tetra calcium aluminate ferrite (Ca₄Al₂Fe₂O₁₀).

N-vinylacetamide and acrylamide, or AMPS[®] and *N,N*-dimethyl acrylamide.^{11–14} Their effectiveness also relies on adsorption on cement.¹⁵ A major drawback of these high molecular weight copolymers ($M_w > 1.5$ mio g/mol) is their pronounced viscosifying effect. This is highly undesirable, because deep wells which exhibit high temperatures require increased slurry densities (1.8–2.3 kg/L) to provide sufficient hydrostatic overburden pressure against the reservoir. Such cement slurries are characterized by low water and high cement content (water-to-cement ratio <0.40). FLAs such as the aforementioned which impact high viscosity to these already viscous cement slurries prompt addition of substantial dosages of dispersants to counteract this thickening effect. Such combinations are uneconomical and present a complicated admixture system. Hence, there is a need for a fluid loss additive with high temperature stable performance and at the same time with minor or no viscosifying effect. By grafting AMPS[®]-NNDMA-AA copolymer blocks onto a humic acid backbone, it was attempted to achieve a fluid loss additive possessing these properties. Additionally, its working mechanism was investigated via measurements of intrinsic viscosity, hydrodynamic size, filter cake permeability, adsorption on cement, and zeta potential. Temperature stability was further probed by exposing the aqueous polymer solution to 150°C (thermal ageing) over a period of 8 h and subsequent polymer characterization and performance testing.

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.¹⁶ Its clinker composition was determined through powder QXRD technique using *Rietveld* refinement (Table I). The amounts of gypsum (CaSO₄·2H₂O) and hemi-hydrate (CaSO₄·0.5 H₂O) present in the cement sample were measured by thermogravimetry. Free lime (CaO) was quanti-

fied following the extraction method established by *Franke*.¹⁷ Using a *Blaine* instrument, the specific surface area was found at 3058 cm²/g. The specific density of this sample was 3.18 kg/L, as measured by Helium pycnometry. Its d_{50} value was 11 μ m.

Silica flour

A commercial sample of silica flour (SSA-1 from Halliburton GmbH, Celle, Germany) containing (wt %) quartz 97.60, CaO 0.57, MgO 0.18, Al₂O₃ 0.17, TiO₂ 0.06 as determined by X-ray fluorescence analysis and LOI 1.40, was used. Its specific surface area (*Blaine method*) was 1857 cm²/g, while the average particle size (d_{50} value) was 32.7 μ m. Specific density of the silica flour was found to be 2.65 kg/L.

Synthesis of the graft copolymer

The humic acid-{AMPS[®]-NNDMA-AA} graft copolymer was prepared by aqueous free radical polymerization using sodium peroxodisulfate as initiator. In a typical reaction, 152 mL of a 14.5 wt % aqueous solution of caustic potash humic acid (pH 9.2, HA 2, Borregaard Lignotech, Sarpsborg, Norway) were placed in a 1 L four-necked flask equipped with a stirrer, thermometer and inlet for N₂ gas. 200 g of water were added into the flask. Prior to the addition of the monomers, the pH of the solution was adjusted to 12 by addition of 13.5 g of sodium hydroxide pellets. Next, 50 g of AMPS[®] (2404 monomer from Lubrizol, Rouen, France), 35 g of NNDMA (Sigma-Aldrich, Munich, Germany) and 1.2 g of acrylic acid (Merck KgaA, Darmstadt, Germany) were added in this order. These proportions result in a molar ratio of 1 : 1.46 : 0.07 between AMPS[®], NNDMA, and acrylic acid, and the ratio between humic acid and the graft monomers is 20 : 80 (wt/wt). Moreover, 0.39 g of EDTA (Sigma-Aldrich, Munich, Germany) and 1 g of defoamer (TEGO ANTIFOAM MR 2123, an organo-modified polysiloxane from Evonik Goldschmidt GmbH, Essen, Germany) were added. While stirring, nitrogen gas was bubbled through the solution for 1 h. Then, the temperature was increased to 50°C and the first amount of Na₂S₂O₈ initiator (5.2 g) was added. After

TABLE II
Characteristic Properties of Humic Acid, Graft Copolymer, Thermally Aged Graft Copolymer and of SCR-500[®] Retarder as Obtained from SEC

Polymer	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)	Brookfield viscosity ^a (mPa s)	$R_{h(z)}$ (nm)	$R_{g(z)}$ (nm)
Humic acid	68,940	21,180	3.3	12	2.8	–
graft copolymer	615,000	192,900	3.2	40	38.1	71.2
aged graft copolymer	283,800	117,600	2.4	22	24.0	48.9
SCR-500 [®] retarder	175,600	108,400	1.6	20	3.0	–

^a Measured in 2.0 wt % solution using Brookfield viscometer model HAT, spindle # H 1 (humic acid) & H 2 (rest of samples).

50 min of reaction time, the second portion of initiator (5.2 g) was added. Grafting was continued for another 70 min while the temperature was increased to 60°C. There, the mixture was left to react for an additional hour before the temperature was again increased to 80°C to complete the reaction within an hour. The reaction was quenched by addition of 6.24 g sodium pyrosulfite (Na₂S₂O₅). The product yields a dark, viscous, odorless liquid which was diluted with 300 mL of DI water. The final product used in this study was a dark brown, 8 wt % aqueous solution possessing low viscosity and a pH value of 5.3. The characteristic properties of the graft copolymer are summarized in Table II.

Synthesis of AMPS[®]-NNDMA-AA copolymer

For comparison, a copolymer of AMPS[®], NNDMA, and acrylic acid was prepared following the procedure for the graft copolymer except that no humic acid was present. Instead, for the initiation process, only 0.94 g of initiator was added for polymerization of the copolymer. The following procedure was identical with that of the graft copolymer. The reaction product was a colorless, 6.2 wt % aqueous solution possessing low viscosity and a pH value of 5.

Retarder

A commercial sample (SCR-500[®]) from Halliburton GmbH, Celle, Germany was used for high temperature retardation of cement. According to literature, this product is prepared by aqueous free radical copolymerization of AMPS[®] and itaconic acid at a molar ratio of 1 : 0.4.¹⁸ The resulting colorless liquid is spray-dried to yield a white powder which was used in this study. The characteristic properties of SCR-500[®] are presented in Table II.

Instruments

Cement characterization

Phase composition of the cement sample was obtained by quantitative X-ray powder diffraction using a Bruker axs D8 Advance instrument from

Bruker, Karlsruhe, Germany with Bragg-Bretano geometry. Topas 3.0 software was employed to quantify the amounts of individual phases present in the sample by following *Rietveld's* method of refinement.¹⁹ The instrument was 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 at a scanning speed of 0.5 s/step (with 0.008°/step). Specific density of the cement sample was measured on an Ultrapycnometer[®] 1000 (Quantachrome Instruments, Boynton Beach, FL/USA). Specific surface area of the sample was determined using a *Blaine* instrument (Toni Technik, Berlin, Germany). The average particle size (d_{50} value) was obtained from a laser-based particle size analyzer (1064 instrument from Cilas, Marseille, France).

Silica flour characterization

Oxide composition of SSA-1 silica flour was determined using an X-ray fluorescence spectrometer (Axios from PANalytical, Almelo, The Netherlands). Specific density, specific surface area, and average particle size (d_{50} value) of the silica sample were measured using the same instrumentation as described above for cement.

Polymer characterization

Viscosity of the polymer solutions was quantified using a *Brookfield* viscometer (Model HAT from Brookfield Engineering Labs, Middleboro, MA/USA) equipped with spindle # H1 or H2. Measurement was carried out at 100 rpm and room temperature. By multiplying the dimensionless reading with the correspondent factor, the values for viscosity (in mPa s) were obtained.

Also, the dynamic viscosities of cement filtrates obtained from the static filtration test were determined. First, kinematic viscosities of cement filtrates containing dosages from 0 to 1.6% bwoc of the graft copolymer were measured at 95°C on an *Ubbelohde* viscometer using 501 10/I, 501 20/II, and 501 30/III capillaries supplied by Schott Instruments, Mainz,

Germany. Totally, 15 mL of filtrate were filled into the reservoir of the capillary and the flow time was measured. From this, the kinematic viscosity of the filtrate was calculated according to eq. (1).

$$v = K (t - \zeta) \quad (1)$$

where K is the viscometer constant ($0.1004 \text{ mm}^2/\text{s}^2$), t is the flow time, and ζ is the flow time dependant *Hagenbach-Couette* correction term, which is provided in the instrument instruction sheet. Multiplying the value obtained for the kinematic viscosity at 95°C with the specific density of the filtrate produced the value for the dynamic viscosity η_{dyn} , as is expressed by eq. (2).

$$\eta_{\text{dyn}} = v \cdot \rho \quad (2)$$

From this, the reduced viscosity of the filtrate η_{red} was calculated according to eq. (3). There, η_0 is the dynamic viscosity of the cement filtrate without polymer and c represents the respective concentration of polymer in the filtrate.

$$\eta_{\text{red}} = \frac{\eta_{\text{dyn}} - \eta_0}{\eta_0 \cdot c} \quad (3)$$

Molecular properties of the graft copolymer and of SCR-500[®] were determined via size exclusion chromatography (SEC). There, a Waters Alliance 2695 (Waters, Eschborn, Germany) separation module equipped with RI detector 2414 (Waters, Eschborn, Germany) and an 18 angle dynamic light scattering detector (Dawn EOS, Wyatt Technologies, Clinton, IA) was employed. The polymers were separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). Aqueous 0.2M NaNO₃ solution (adjusted with 50 wt % aqueous NaOH to pH 9) was used as an eluant at a flow rate of 1.0 mL/min. FLA solution (concentration: 10 mg/mL) was filtered through a 5- μm filter. A d_n/d_c value of 0.156 mL/g (value for polyacrylamide²⁰) was used for calculation of M_w and M_n . Hence, the molecular weights measured are relative to polyacrylamide. Characterization of humic acid was carried out on another separation module (Waters Alliance 2695) equipped with RI detector 2414 and a 3 angle dynamic light scattering detector (mini Dawn from Wyatt Technologies, Santa Barbara, CA). The humic acid solution was filtered through a 0.2- μm filter and then separated on a UltrahydrogelTM precolumn and three UltrahydrogelTM columns (120, 250, and 500; Waters, Eschborn, Germany). Eluent was 0.1M aqueous NaNO₃ solution (adjusted to pH 12.0 with NaOH) pumped at a flow rate of 1.0 mL/min. The value of d_n/d_c used to calculate M_w and M_n for humic acid was 0.218 mL/g (value for lignin).²¹

The specific anionic charge amounts of the polymers used in this study were determined at room temperature in deionized water, 0.1M NaOH (pH 12.6) and cement pore solution, using a PCD 03 pH apparatus (BTG Mutek GmbH, Herrsching, Germany). Cement pore solution was freshly prepared by vacuum filtration of neat API Class G cement slurry (w/c ratio 0.44) using blue ribbon filter paper and a diaphragm vacuum pump (Vacuubrand GmbH, Wertheim, Germany). Charge titration was carried out according to a literature description employing a 0.001N solution of laboratory grade poly (diallyl dimethylammonium chloride) from BTG Mutek GmbH, Herrsching, Germany as cationic polyelectrolyte.²² The values presented are the averages obtained from three different measurements. The standard deviation of this method was found to be $\pm 5 \text{ C/g}$.

Thermal stability of the graft copolymer and the humic acid backbone was compared using thermogravimetric analysis (instrument STA 409 CD, NETZSCH Geraetebau GmbH, Selb, Germany) under nitrogen atmosphere at a heating rate of 10°C per min. Prior to analysis, aqueous solutions of the graft copolymer and of humic acid were dialyzed for 2 days using a Spectra/Por[®] dialysis membrane (MWCO 50,000) from Spectrum Laboratories, Rancho Dominguez, CA. The dialyzed copolymer and humic acid solutions were freeze dried and the polymer powders thus obtained were used. For thermal ageing of the graft copolymer, an OFITE roller oven was used. There, 300 mL of the graft copolymer solution were poured into a 500 mL teflon liner (OFITE part # 175 - 60) and placed into a stainless steel grade 316 ageing cell (OFITE part # 175 - 60). A pressure of 7 bar was applied to the cell which was rotated at 25 rpm in the roller oven. The oven was then heated up to a temperature of 150°C and left rotating for 8 h. After this time, the cell was removed from the oven and cooled with water to room temperature.

Cement slurry preparation

Cement slurries were prepared in accordance with the procedures set forth in *Recommended Practice for Testing Well Cements*, API Recommended Practice 10B, issued by the American Petroleum Institute, using API Class G oil well cement and deionized water.²³ At first, the cement was dry blended with silica flour at a weight ratio of 65: 35 to avert cement compressive strength retrogression occurring at temperatures above 115°C . This blend was mixed with DI water at a water-to-cement (w/c) ratio of 0.57 and a water-to-solids (w/s) ratio of 0.41 (solids = cement + silica flour) using a blade-type laboratory blender manufactured by Waring Products Inc. (Torrington,

CT). Generally, the graft copolymer solution was dissolved in the mixing water while powdery SCR-500[®] retarder was dry blended with cement. All admixture dosages are given in % by weight of cement (bwoc). In a typical experiment, the amount of mixing water required to achieve a w/c ratio of 0.57 excluding the amount of water present in the copolymer solution was placed in the cup of the Waring blender. This was followed by addition of the exact volume of copolymer solution holding the desired amount of copolymer. The cement: SSA-1 blend (65:35 wt %) was added within 15 s to the mixing water at 4000 rpm. Thereafter, stirring continued for additional 35 s at 1200 rpm. To ensure sufficient homogenization after mixing, all slurries were poured into a 500-mL slurry container and stirred for 20 min at 95°C in an atmospheric consistometer (model 1250 from Ametek Chandler Engineering, Broken Arrow, OK).

Rheology of the cement slurries was determined following API RP 10B procedure employing a model PVS Rheometer from Brookfield Engineering Laboratories, Middleboro, USA. This rheometer is capable of measuring viscosity at elevated temperatures above 100°C. Totally, 30 mL of the cement slurry homogenized in the atmospheric consistometer were poured into the rheometer cup. A pressure of 500 psi was applied and the sample was heated to 150°C. Thereafter, the shear stress (lbs/100 ft²) was measured at shear rates of 1022, 511, 341, 170, 10.2, and 5.1 s⁻¹ respectively using bob B5.

High temperature high pressure consistometer

HTHP thickening times of cement slurries were measured at 150°C under an applied pressure of 400 bar using a consistometer model 8240 (Ametek Chandler Engineering, Broken Arrow, OK). The cement slurries holding specified admixture dosages were prepared as described above, but without homogenization in the atmospheric consistometer. The slurries were poured into the HTHP consistometer cell and the time to reach 70 Bc (Bearden unit of consistency, a dimensionless unit) was taken as the cement slurry thickening time.

API static fluid loss

Static fluid loss at 150°C was measured using a 500-mL high pressure, high temperature (HP/HT) stainless steel filter cell manufactured by OFI Testing Equipment (Houston, TX). Design of this HP/HT filter cell and its operation are described in detail in a norm issued by the American Petroleum Institute (API).²³ After pouring the homogenized slurry obtained from the atmospheric consistometer at 95°C into the HT/HP cell preheated to 90°C, a condenser

was attached to the filtrate collecting valve and a differential pressure of 70 bar N₂ was applied at the top of the cell. Within 40 min, the temperature was increased to the test temperature of 150°C using a heating jacket (OFI Testing Equipment, Houston, TX). Filtration proceeded through a 22.6 cm² (3.5 in²) mesh metal sieve placed at the bottom of the cell. The fluid volume collected within 30 min was doubled as described by API RP 10B and regarded as API fluid loss of the corresponding cement slurry. The values reported for the respective API fluid loss test represents the average obtained from three separate measurements. Maximum deviation of individual values in the fluid loss tests was ±10 mL/30 min. Where complete dehydration of the cement slurry in <30 min occurred, the valve of the condenser was occasionally opened to ascertain the dehydration time.

Adsorption

The adsorbed amount of admixture (graft copolymer or retarder) was determined from the cement filtrate collected in the respective fluid loss test. Generally, the depletion method was applied, i.e., it was assumed that the decrease in the polymer concentration before and after contact with cement solely resulted from interaction with cement, and not from insolubility of the polymer. This assumption was confirmed through a solubility test. For this purpose, 35 g/L of the graft copolymer and of the retarder respectively (this concentration correlates to a polymer dosage of 2.0% bwoc) were dissolved in cement pore solution and stored for three days. No precipitation was observed. The amount of individual polymer retained was calculated from the difference in the equilibrium concentration of the polymer present in the liquid phase before and after contact with cement (depletion method). A High TOC II apparatus (Elementar, Hanau, Germany) equipped with a CO₂ detector was used for quantification of the carbon content present in the solutions. Maximum deviation of the adsorbed amount was found at ±0.1 mg polymer/g cement. Quantification of adsorbed amounts of the individual polymers was done as follows: Since the retarder is colorless while the graft copolymer is dark brown, UV-vis spectroscopy was used to determine the graft copolymer concentration while adsorbed amount of retarder was obtained by subtracting the carbon content originating from the graft copolymer from the total organic carbon content found in the filtrate and converting this value into concentration of retarder. For this purpose, a standard addition plot of both polymer solutions holding a fixed dosage of 0.029% bwoc (0.5 g/L) retarder and increasing dosages of graft copolymer was taken at 600 nm using a spectrofex 6100 spectrophotometer (WTW Wissenschaftlich-Technische

TABLE III
Standard Addition Plot of UV-Vis Absorbance
Measured at 600 nm and at Increased Dosages of Graft
Copolymer at a Fixed Dosage of 0.029% bwoc (0.5 g/L) of
SCR-500[®] Retarder

Graft copolymer dosage (g/L)	Absorbance @ 600 nm
0.5 graft copolymer only (w/o retarder)	0.491
0.0	-0.001
0.5	0.496
1.0	1.019
1.5	1.463

Werkstätten GmbH, Weilheim, Germany). This standard plot of absorbance vs. graft copolymer concentration was used to determine the concentration of the copolymer based on the equation $y = 0.983x + 0.007$ ($R^2 = 0.999$). Where y represents the absorbance, x the concentration of the graft copolymer, and R is coefficient of determination. The data for the standard plot are given in Table III.

Zeta potential measurement

Titration of the graft copolymer to the cement/silica flour slurry (c : s = 65 : 35 wt/wt) was performed at room temperature on an electro acoustic spectrometer (DT-1200 from Dispersion Technology, Bedford Hills, NY). Immediately after mixing the slurries were poured into the cup of the spectrometer and measured without homogenization in the atmospheric viscometer. The resulting zeta potential values were recorded and the accuracy of this method was ± 1 mV.

RESULTS AND DISCUSSION

Properties and structure of the graft copolymer

The synthesized graft copolymer was first dialyzed and then characterized by size exclusion chromatog-

raphy (Fig. 1). According to this analysis, the graft copolymer exhibits a significantly higher molar mass ($M_w \sim 600,000$ g/mol) than the humic acid backbone ($M_w \sim 69,000$ g/mol), thus confirming successful grafting (Table II). In accordance with this finding, the particle size (hydrodynamic diameter) as determined by size exclusion chromatography increased from 5.6 nm for the unmodified humic acid to ~ 80 nm after the grafting reaction. Similarly, the Brookfield viscosity of a 2 wt % aqueous solution shows a substantial increase for the graft copolymer in comparison to that of individual humic acid. Finally, elemental analysis confirmed the incorporation of N and S containing monomers into the graft copolymer. The difference between calculated and actual elemental composition of the graft copolymer is attributed to the removal of impurities, unreacted monomers and salts during dialysis. Also, the elemental analysis data provided in Table IV suggest that relative to the feeding molar ratios, only 87.5% of AMPS[®], 92.4% of NNDMA, and 19.6% of acrylic acid fed were incorporated into the graft copolymer. Hence, the actual molar composition of the graft chain is 1 : 1.54 : 0.02. This differs from the feeding molar ratio which was 1 : 1.46 : 0.07.

According to literature, the phenolic group present in humic acid allows grafting of monomers through a hydrogen abstraction mechanism initiated by strong oxidants such as e.g., peroxodisulfates or Ce^{4+} . For example, acrylic acid and other monomers have been demonstrated to graft well onto humic acid or caustic lignite (the latter possesses some building blocks which are similar to these contained in humic acid).²⁴⁻²⁹ Successful occurrence of grafting was confirmed by SEC data and performance testing. The copolymer made from AMPS[®], NNDMA and acrylic acid only (no humic acid present!) under identical conditions with those for the graft copolymer exhibits a molecular size as expressed by the

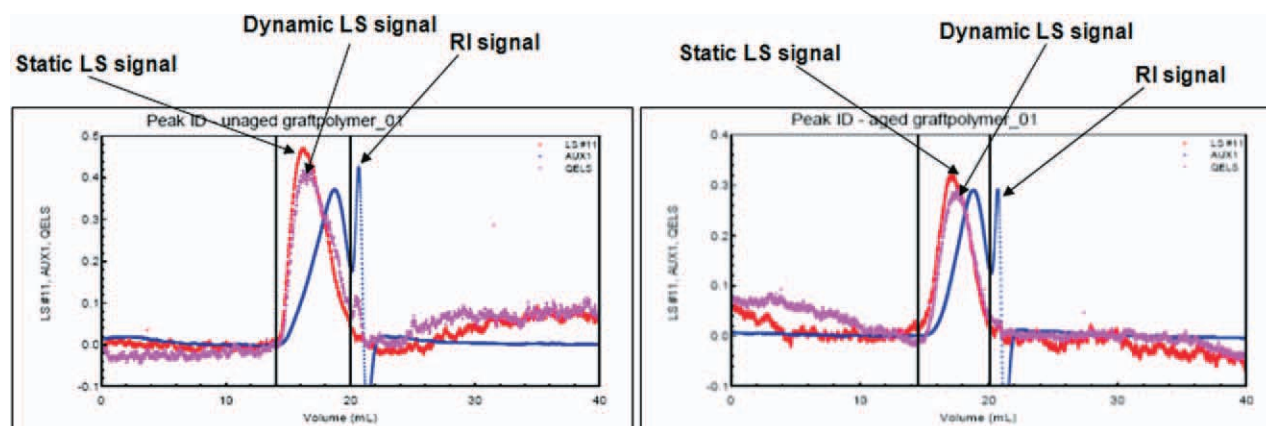


Figure 1 Size exclusion chromatograms of graft copolymer as obtained from synthesis (left) and after ageing for 8 h @ 150°C (right); eluent: 0.2M NaNO₃, pH = 9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Elemental Analysis Data for Graft Copolymer, Humic Acid, and Graft Chain

Elements	Graft copolymer found (%)	Graft copolymer calculated (%)	Humic acid found (%)	Graft chain calculated (%)
C	39.0	43.4	38.7	44.9
H	7.0	6.0	3.7	6.6
O	36.0	27.1	41.5	23.2
N	6.6	7.3	1.0	8.9
S	6.0	6.8	0.8	8.2
Na	4.9	6.7	0.5	8.3
K	0.5	2.8	13.8	-

O content always calculated as difference to 100 %.

$R_{g(z)}$ value which is considerably smaller than that of the graft copolymer (21.2 nm for the copolymer vs. 71.2 nm for the graft copolymer). Thus, it is evident that the graft copolymer possesses a larger number of side chains. Additionally, fluid loss performance of the graft copolymer at 150°C in cement slurry was compared with that of a mere blend of humic acid with the AMPS[®]/NNDMA/AA copolymer at a 20:80 wt ratio. There, the graft copolymer produced an excellent API fluid loss of 25 mL whereas the blend showed practically no fluid loss control (~ 200 mL) for the cement slurry. This experiment demonstrates that under the conditions selected, indeed a reaction between humic acid, AMPS[®], NNDMA, and acrylic acid had occurred and that not just a simple mixture of humic acid and an AMPS[®]/NNDMA/AA copolymer is present. Accordingly, the graft copolymer is composed of a humic acid backbone and AMPS[®]-*co*-NNDMA-*co*-AA graft chains which are linked to the backbone via oxygen atoms from phenol groups (Fig. 2). Note that the chemical formula used there for humic acid was taken from

literature.³⁰ With humic acid being a natural polymer, variations in its composition may occur.

Using thermogravimetric analysis and data from SEC, an attempt was made to develop a more precise structural model for the graft copolymer. Thermogravimetry revealed that at incremental increase of temperature, individual humic acid shows a gradual and almost linear decomposition with temperature (Fig. 3). Opposite to this, after an initial loss of ~ 6.5% water, the graft copolymer shows very high resistance to degradation up to a temperature of ~ 380°C. Beyond this temperature, rapid breakdown of the graft copolymer occurs. Obviously, humic acid present in the graft copolymer is protected from thermal degradation by the lateral graft chains made of AMPS[®]-NNDMA-acrylic acid. The overall architecture of the graft copolymer is that of a stretched backbone worm, as is illustrated in Figure 4. There, the graft chains present the teeth of a rather linear main chain. A similar model has been proposed for the solvated conformation of polycarboxylate comb polymers bearing polyethylene oxide

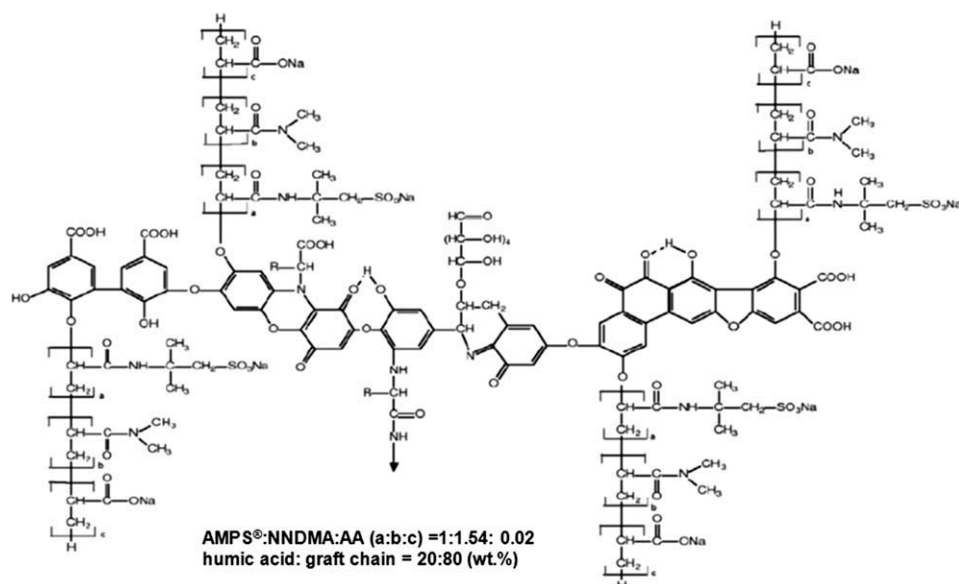


Figure 2 Structural representation of synthesized graft copolymer; structure of humic acid after.³⁰

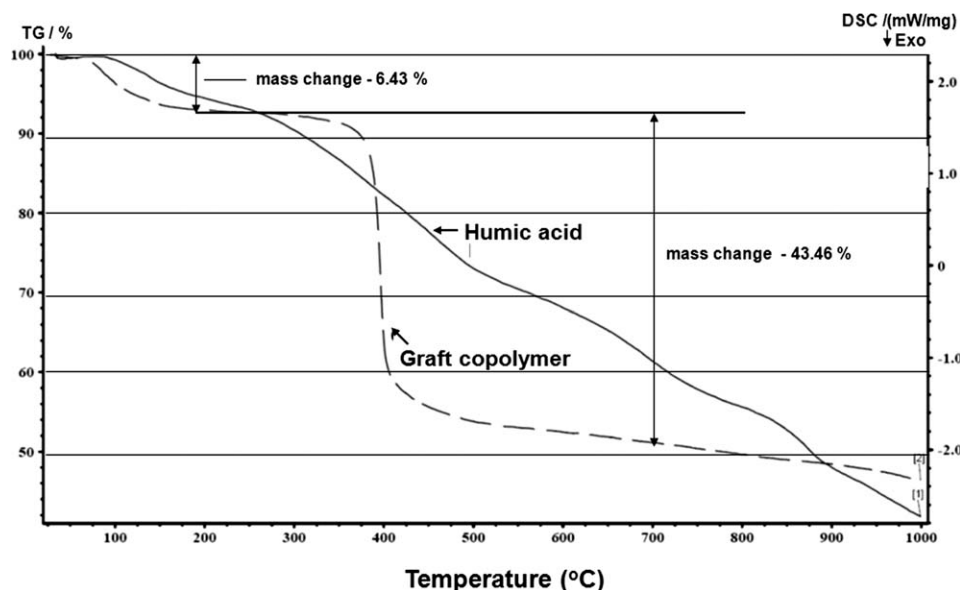


Figure 3 Thermogravimetric analysis of the humic acid backbone and of the graft copolymer.

graft chains (sodium polymethacrylate-*g*-PEO comb copolymers).^{31–33} This specific structure is believed to be responsible for the superior thermal stability of the graft copolymer.

Another evidence for the existence of a stretched backbone worm structure is provided by data obtained from SEC. There, a value of ~ 1.8 was obtained for the ratio of R_g/R_h (the so-called *Burchard* parameter). According to *Burchard*, values of 1.5–2.05 represent linear molecules, while at >2.2 , stiff chains exist.³⁴

Fluid loss performance of the graft copolymer

At first, the dosage of SCR-500[®] retarder required to delay the set of cement sufficiently to obtain slurry which is fluid and pumpable over several hours was determined. The target was to achieve a thickening time (pumping time) at 150°C for at least 4 h.

Static filtration properties of cement/silica flour slurries containing increased dosages (0–1.6% bwoc) of the graft copolymer and a fixed dosage of 1.2% bwoc of SCR-500[®] retarder were determined at 150°C (slurry density 1.93 kg/L). The results are shown in Figure 5.

Generally, API fluid loss decreases exponentially with increasing graft copolymer dosage. The minimum concentration of FLA needed to achieve an API fluid loss below 100 mL/30 min lies at 0.8% bwoc. This value presents a relatively low dosage, considering the harsh temperature conditions. In comparison, conventional CaAMPS[®]-NNDMA copolymers which are routinely used on HTHP wells require substantially higher dosages to achieve the same fluid loss as will be shown later in Table VI. The graft copolymer reaches its maximum

effectiveness at a dosage of 1.2 % bwoc. From there, a filtrate volume of less than 30 mL/30 min is achieved. In a separate test, SCR-500[®] retarder was found to provide no fluid loss control at all (slurry dehydration occurred in less than 2 min). Thus, it was confirmed that filtration control was solely the effect of the graft copolymer.

Effect on rheology

Table IV presents results on the viscosifying properties of the synthesized graft copolymer in the presence of SCR-500[®] retarder. It shows that the graft copolymer generally increases slurry viscosity, but much less than conventional synthetic FLA polymers such as e.g., CaAMPS[®]-NNDMA copolymer.¹⁵ Thus,

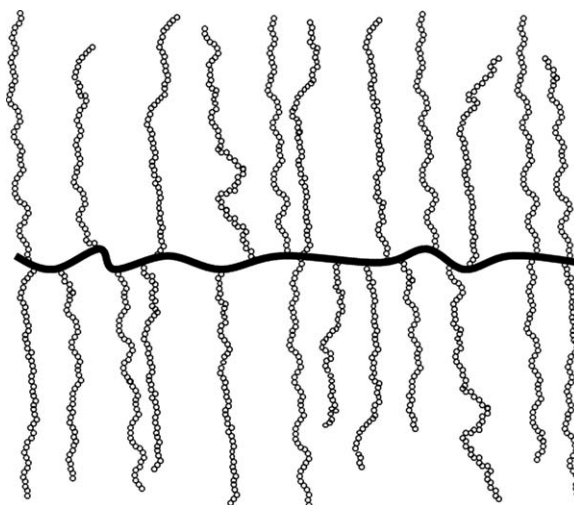


Figure 4 Model of the synthesized graft copolymer exhibiting the structure of a stretched backbone worm decorated with lateral graft chains.

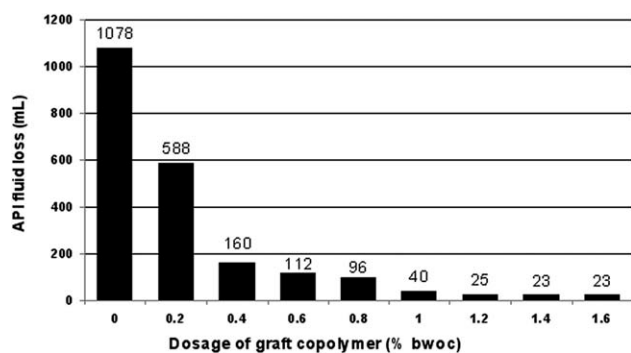


Figure 5 API fluid loss of Class G cement/silica (65:35% wt./wt.) slurries containing increased dosages of graft copolymer and 1.2% bwoc of SCR-500[®] retarder, measured at 150°C.

the graft copolymer behaves more advantageous in high density cement slurries. Still, caution needs to be exercised when the dosage of this FLA exceeds $\sim 1.5\%$ bwoc. Fortunately, such excessive dosages are not required to achieve sufficient fluid loss control with this polymer.

High temperature stability

To ascertain the high temperature stability of the graft copolymer, a sample of the aqueous solution was exposed at 150°C for 8 h in a roller oven and subsequently used in a static filtration test at 150°C. The results are presented in Table V. Interestingly, the same API fluid loss values were obtained for the graft copolymer before and after thermal exposure. This result instigates that the graft copolymer is high temperature stable with respect to fluid loss performance, while the rheology of its aqueous solution (Table II) and of the cement slurry (Table V) is lower in comparison to that of the unaged sample. This

effect is owed to partial depolymerization of the graft copolymer, as was evidenced by size exclusion chromatography (see Fig. 1 and Table II). The molecular weights of the aged FLA were reduced by $\sim 40\%$ as a result of thermal exposure. This effect also became apparent from the Brookfield viscosity of their aqueous solutions and a reduction in the steric size (R_h) of the solvated macromolecule (see Table II). Also, the aged graft copolymer solution exhibited a lighter color than the unaged sample. From this observation it was concluded that the humic acid was partially oxidized and fragmented while the graft chains remained essentially unaffected. In spite of this partial depolymerization, the graft copolymer still maintained its high effectiveness as cement fluid loss additive.

Mechanistic study

To uncover the working mechanism of this graft copolymer as fluid loss additive, a series of experiments were devised. First, the correlation between API fluid loss, filter cake permeability, dynamic filtrate viscosity, and filtercake pore size obtained at 150°C in the presence of varied dosages (0–1.6% bwoc) of the graft copolymer and of 1.2% bwoc of retarder was studied. The results are presented in Table VI. The dynamic filtrate viscosity was found to be always very low and independent of dosage. This means that filtrate viscosity has no impact on the fluid loss performance of the graft copolymer whereas filter cake permeability decreases linearly with API fluid loss. For example, permeability decreases from 1044 μD to 2.2 μD while API fluid loss is reduced from 1078 mL to 25 mL/30 min (see Table VI). This clearly emphasizes that the graft copolymer works by reduction of filter cake permeability.

TABLE V
Rheology (Shear Stress) of API Class G Cement/Silica Slurries Containing 0–1.6% bwoc of the Graft Copolymer and 1.2% bwoc of SCR-500[®] Retarder, Measured at 150°C and at Different Shear Rates

Graft copolymer dosage (% bwoc)	Shear stress (lbs/100 ft ²) at shear rate (rpm) @ 150°C					
	300	200	100	6	3	600
0.0 ^a	60	40	17	1	0	115
0.2 ^a	55	30	11	1	0	98
0.4 ^a	50	36	13	2	1	99
0.6 ^a	57	38	16	2	1	109
0.8	90	68	54	5	4	152
1.0	168	106	57	7	6	268
1.2	181	126	70	10	8	>300
1.4	>300	245	130	19	17	>300
1.6	>300	>300	211	30	25	>300
For comparison: CaAMPS [®] -NNDMA copolymer ¹⁵						
0.5	92	70	41	2	2	176
0.8	154	110	71	6	4	274
1.0	199	136	83	9	6	>300

^a Low viscosity of the cement slurry causes solids settling.

TABLE VI
Rheology (Shear Stress) and API Fluid Loss of API Class G Cement/Silica Slurries Containing 1.2% bwoc of the Graft Copolymer Before and After Thermal Exposure to 150°C over 8 h^a

Graft copolymer	300	200	100	6	3	600	API fluid loss @ 150°C (mL)
Unaged	181	126	70	10	8	>300	25
Aged 8 h @ 150°C	123	70	35	2	1	220	24

^a Slurry also includes 1.2% bwoc of SCR-500[®] retarder.

To probe the reason behind the reduction in filter cake permeability, adsorption of the graft copolymer on the cement/silica solids was investigated.

Adsorption of the graft copolymer

Since the graft copolymer is an anionic polyelectrolyte similar to AMPS[®]-*co*-NNDMA fluid loss additive which exhibits an adsorptive working mechanism,¹⁵ it was speculated that this graft copolymer may function according to the same principle. Thus, adsorbed amounts of the graft copolymer and of the retarder were determined by UV-vis spectroscopy and TOC measurement, as described in the experimental section. The results are displayed in Figure 6.

Generally, the adsorbed amount of the retarder is quite constant (variation range 5.4–7.1 mg/g of cement) and is independent of its dosage and that of the graft copolymer. While the adsorbed amount of the graft copolymer clearly increases with dosage. The adsorbed amount first increases linearly until it levels out at a dosage of ~ 1.5% bwoc. There, a saturated adsorbed amount of ~ 15 mg/g cement was observed. This behavior is best described by a Langmuir type adsorption isotherm which includes monolayer formation of the adsorbed polymer.

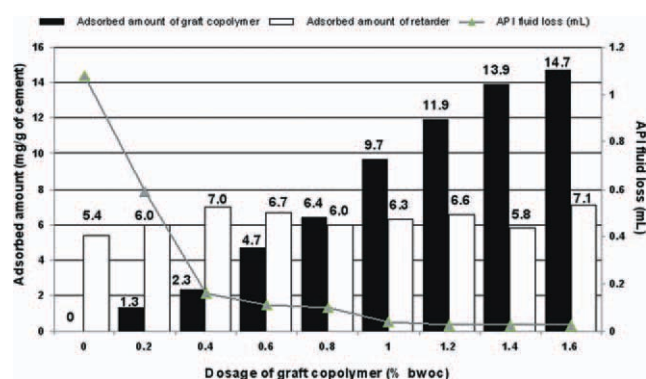


Figure 6 Adsorbed amounts of graft copolymer and retarder respectively and corresponding API fluid loss of the cement/silica slurry holding 1.2% bwoc of retarder as a function of graft copolymer dosage, measured at 150°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Adsorption was confirmed to be the sole reason for FLA depletion through a solubility test. For this purpose, 2% bwoc of the graft copolymer were dissolved in this cement pore solution and left to rest for 3 days. No precipitation of the FLA was observed after this period.

Another observation from Figure 6 is that the adsorbed amount of FLA still increases even when API fluid loss remains stable below 30 mL. This effect can be explained as follows: API filtrates of <30 mL/30 min are produced by dehydration of the first layers of the cement slurry next to the sieve. Formation of this early filtrate (the “spurt loss”) is always necessary to produce a filter cake which is tight and seals the slurry against further dehydration. There is no possibility to avoid this initial spurt loss. Thus, using this test protocol, it is impossible to achieve API fluid loss values of less than 25 mL/30 min.

Next, the adsorptive working mechanism of the FLA was further investigated via zeta potential measurement and determination of its calcium binding capacity.

Zeta potential measurement

The zeta potential curve obtained for the cement/silica flour slurry under titration of the graft copolymer solution is displayed in Figure 7. Without copolymer, the slurry exhibits a positive charge of ~ +4 mV. Stepwise addition of the anionic graft copolymer reverses the positive charge to negative values until a point of saturation is achieved. This trend towards negative charges confirms that polymer adsorption onto the surfaces of cement and silica occurs.³⁵

Specific anionic charge and calcium binding capacity

For the unaged graft copolymer, aged graft copolymer, and humic acid, their specific anionic charges in deionized water, 0.1M NaOH (pH 12.6) and cement pore solution were determined. The results are exhibited in Figure 8.

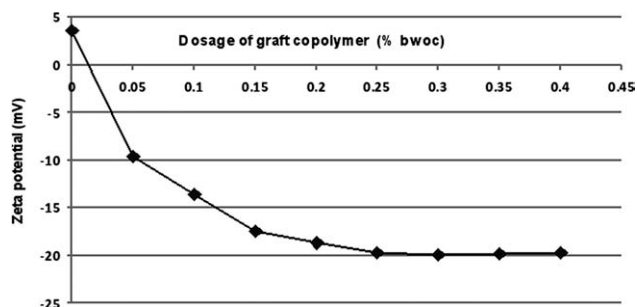


Figure 7 Zeta potential of cement/silica slurry titrated with increased dosages of graft copolymer.

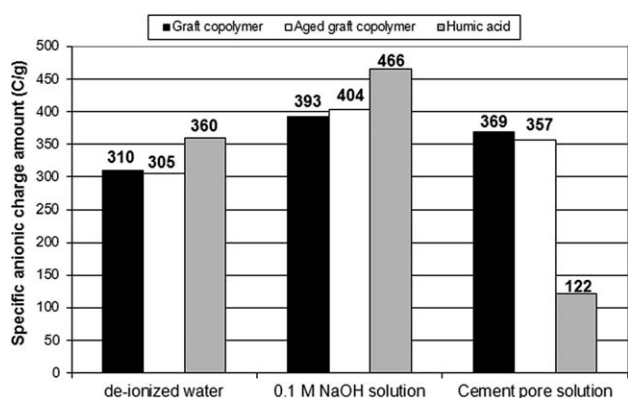


Figure 8 Specific anionic charge amounts of the graft copolymer, aged graft copolymer, and humic acid in DI water, 0.1M NaOH (pH 12.6) and cement pore solution.

Generally, in all fluid systems, the aged and unaged graft copolymers exhibit comparable anionic charge amounts. This again indicates that during the ageing process, the humic acid backbone is fragmented while no significant degrafting of side chains takes place. Additionally, all samples exhibit higher specific anionic charge amounts in 0.1M NaOH than in DI water. This effect is owed to increased deprotonation at high pH. Whereas in cement pore solution (which contains ~ 0.6 g/L of Ca^{2+}), anionic charges of all samples dropped, with the effect on humic acid being particularly strong. A possible explanation for this behavior is strong calcium complexation.²²

To probe into this, the calcium binding capacities of humic acid and of aged and unaged graft copolymer were determined in NaOH (pH 12.6) in presence and absence of 0.6 g/L Ca^{2+} ions (Table VII). It was found that the specific anionic charge amount

TABLE VII
API Fluid Loss, Dynamic Filtrate Viscosity, and Filter Cake Permeability of Cement/Silica Flour Slurries Containing Different Dosages of Graft Copolymer and 1.2% bwoc of SCR-500[®] Retarder, Measured at 150°C

Graft copolymer dosage (% bwoc)	Dynamic filtrate viscosity (mPa·s)	Filtercake permeability (μD)	API fluid loss (mL)
0.0	0.44	1044	1078 ^a
0.2	0.39	448	588 ^a
0.4	0.41	96	160
0.6	0.45	50	112
0.8	0.63	71	96
1.0	0.48	5.1	40
1.2	0.49	2.2	25
1.4	0.49	2.0	23
1.6	0.50	2.0	23
For comparison: CaAMPS [®] -NNDMA copolymer ¹⁵			
0.8	4.3	4,905	554 ^a
1.0	6.0	4,432	410 ^a

^a Calculated (dehydration occurred in less than 30 min).

of humic is most strongly affected by Ca^{2+} (reduction of 84%). At this Ca^{2+} concentration of 0.6 g/L, humic acid partially comes out of solution as a brown precipitate consisting of calcium humate. While for the unaged and aged graft copolymers, the specific anionic charge amounts only decrease by 12% and 28% respectively, with no precipitation. This signifies much lower calcium binding capacity for the graft copolymers. For comparison, the anionic charge of CaAMPS[®]-NNDMA copolymer is reduced by 4% only.³⁶ This instigates that the interaction between Ca^{2+} and the graft copolymer mainly occurs at the humic acid backbone and less at the lateral chains.

The experiments demonstrate that the grafting process produces a copolymer with greatly enhanced solubility in the presence of Ca^{2+} . This property is a prerequisite for the effectiveness of the graft copolymer in cementitious systems.

Additionally, the graft copolymer is fully compatible and effective with a synthetic retarder based on AMPS[®]-*co*-itaconic acid. They do not perturb each other, which differentiates it from other cement fluid loss additives such as e.g., CaAMPS[®]-*co*-NNDMA.³⁷

The adsorptive mechanism of the graft copolymer is highly surprising since it is well known that ettringite, a cement hydrate formed from tricalcium aluminate and calcium sulfate present in cement, presents the main mineral for adsorption of anionic admixtures.³⁸ However, ettringite is not stable at temperatures exceeding $\sim 80^\circ\text{C}$ and therefore is practically absent at 150°C which was the test temperature here. Therefore, the graft copolymer has to adsorb onto another mineral substrate which most likely are calcium silicate hydrates. In cement pore solution they were found to develop a slightly positive charge which increases with temperature as a result of increased Ca/Si ratio.³⁹ This effect renders them a potential substrate for polymer adsorption.

TABLE VIII
Specific Anionic Charge Amount of Humic Acid, Unaged, and Aged Graft Copolymer Respectively, Measured in 0.1M NaOH (pH 12.6) in Presence and Absence of 0.6 g/L Ca^{2+} Ions

Polymer	Specific anionic charge amount (C/g)		Reduction of anionic charge by Ca^{2+} ions
	NaOH @ pH 12.6	NaOH @ pH 12.6 plus 0.6 g/L Ca^{2+}	
Humic acid	466	76	84%
Graft copolymer	393	345	12%
Aged graft copolymer	404	293	28%
CaAMPS [®] -NNDMA copolymer ^{15,38}	368	352	4%

CONCLUSIONS

Monomers of AMPS[®], NNDMA, and acrylic acid were successfully grafted on humic acid, as was evidenced by SEC analysis (R_g value) and comparative performance testing of the graft copolymer and a mere blend of humic acid with an AMPS[®]/NNDMA/AA copolymer prepared under similar conditions as the graft copolymer. The latter provided excellent fluid loss control while the blend showed no fluid loss control at all. The working mechanism of humic acid-{AMPS[®]-*co*-NNDMA-*co*-AA} graft copolymer as cement fluid loss additive was found to rely on reduction of filtercake permeability. This reduction is achieved by adsorption of the graft copolymer on cement and possibly silica particles. Adsorption was evidenced by zeta potential measurement showing increased negative loading onto solid particles present in the cementing formulation. Through strong adsorption which is hardly affected by temperature, the polymer constricts the pores of the filter cake. The study also shows that this graft copolymer exhibits only a moderate viscosifying effect on the cement slurry, and thus qualifies for high density slurries which are required on high temperature high pressure wells. Additional research is in progress to validate which cementitious phases are responsible for the adsorption of the graft copolymer.

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