

Working Mechanism of a High Temperature (200°C) Synthetic Cement Retarder and Its Interaction with an AMPS[®]-Based Fluid Loss Polymer in Oil Well Cement

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ABSTRACT: A copolymer comprising of 2-acrylamido-2-methyl propane sulfonic acid (AMPS[®]) and itaconic acid (molar ratio 1 : 0.32) was synthesized by aqueous free radical polymerization and probed as high temperature retarder for oil well cement. Characteristic properties of the copolymer including molar masses (M_w and M_n), polydispersity index and anionic charge amount were determined. The copolymer possesses a M_w of $\sim 2 \times 10^5$ g/mol and is highly anionic. HT/HP consistometer tests confirmed effectiveness of the retarder at temperatures up to 200°C. The working mechanism of NaAMPS[®]-*co*-itaconic acid was found to rely exclusively on its huge calcium binding capacity (5 g calcium/g copolymer). It reduces the amount of freely dissolved, nonbound calcium ions present in cement pore solution and thus hinders the growth of cement hydrates because of lack of calcium. The value for the calcium binding capability is 46 times higher than the stoichiometric amount per —COO^- functionality. Con-

sequently, calcium also coordinates to other donor atoms present in the retarder. NaAMPS[®]-*co*-itaconic acid also adsorbs onto cement, as was evidenced by TOC analysis of cement filtrates, zeta potential measurement and decreased rheology of cement pastes. However, adsorption plays no role in the retarding mechanism of this copolymer. Combination of NaAMPS[®]-*co*-itaconic acid retarder with a common CaAMPS[®]-*co*-NNDMA fluid loss additive (FLA) revealed that competitive adsorption on cement between these two admixtures occurs. The retarder fills interstitial adsorption sites on cement located between those occupied by the larger FLA molecules. In consequence, fewer amounts of CaAMPS[®]-*co*-NNDMA can adsorb and its effectiveness is reduced. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4772–4781, 2012

Key words: oil well cement; AMPS[®] copolymer; retarder; fluid loss additive; high-temperature polymer

INTRODUCTION

The cementing of oil and gas wells is one of the most important and challenging operations performed in the construction of a well bore. The difficulty lies in the high pressures and temperatures occurring in deep boreholes, which make it very hard to control the properties of the cement slurry. To ensure a cement seal, which is impermeable to gases and fluids, additives are included into the slurry formulation.¹ For example, retarders are useful to delay the setting time of the slurry and thus to provide sufficient pumpability time over long distances.² However, once the cement slurry is in place, immediate hardening and strength development is desirable to minimize rig cost resulting from extended wait on cement times.

Five principal concepts have been proposed for the working mechanism of cement retarders:² The first one is designated “adsorption theory.” Here, the retarder adsorbs onto the surfaces of cement, thereby acting as a barrier for continued contact with water.³ The second model involves calcium complexation. There, the retarder reduces the concentration of free calcium ions existing in pore solution either by forming insoluble precipitates or by chelating the calcium ions, thus preventing the formation of cement hydrates such as, for example, ettringite.⁴ Another potential mechanism is nucleation poisoning. Here, the retarder occupies the reactive faces of initially formed nano nuclei of cement hydrates and inhibits their growth.⁵ The fourth mechanism is referred to as protective layer formation. A semipermeable membrane is formed on the surface of cement particles, which decelerates the migration of water to the mineral surface. Eventually, the protective coating and the layer burst because of the high pressure created by osmosis driven diffusion. Subsequently, hydration continues at a normal rate.⁶ The last mechanism involves a dissolution–precipitation process. At first, dissolution of

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TABLE I
Phase Composition (QXRD, 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 ·2 H 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 (μm)
59.6	22.8	1.2	13.0	< 0.3	2.7 ^a	0.0 ^a	0.7	3.18	3058	11

C₃S: tricalcium silicate (Ca₃(SiO₄)O); C₂S: dicalcium silicate (Ca₂SiO₄); C₃A_c: cubic modification of tricalcium aluminate (Ca₉Al₆O₁₈); C₄AF: tetra calcium aluminate ferrite (Ca₄Al₂Fe₂O₁₀).

^a Measured by thermogravimetry.

calcium ions is enhanced by extraction, for example, with organic phosphonic acids. Thereafter, a layer of calcium phosphonate precipitate is formed, which binds to the surface of cement, thus creating a diffusion barrier to water and inhibiting the nucleation.⁷

An important class of retarders is hydroxycarboxylic acids such as citric and tartaric acid. They are effective up to a temperature of ~ 95°C only.² In 1999, a novel synthetic retarder for high temperatures comprised of 2-acrylamido-2-methyl propane sulfonic acid (AMPS[®]) and itaconic acid was presented by Rodrigues.⁸ Very recently, a terpolymer, which also contains AMPS[®] and itaconic acid and additional N-vinyl-2-pyrrolidone as comonomer was reported to retard cement slurries effectively at temperatures up to 130°C.⁹ In spite of the huge importance in the construction of deep wellbores, the principle working mechanism of these AMPS[®]-*co*-itaconic acid cement retarders remained unclarified to this day.

In oil well cementing, most often a combination of additives is used to achieve optimal slurry properties. One important group of additives includes fluid loss additives (FLAs). These admixtures prevent uncontrolled loss of water from the cement slurry while it is being pumped along porous formations. AMPS[®]-NNDMA-based copolymers have been shown to reduce filter cake permeability by adsorption onto the positively charged surfaces of cement hydrates.^{10,11} This way, good fluid loss control of the slurry is achieved. However, through multiple ways of interaction additives can influence each other positively or negatively in their performance. Some of these interactions have been presented in recent works.^{12,13}

The aim of this investigation was to clarify the working mechanism of a high temperature stable NaAMPS[®]-itaconic acid copolymer as retarder for oil well cements. For this purpose, slurry thickening time at high temperatures, rheology, zeta potential, adsorbed amount on cement and the anionic charge amount of the copolymer were determined. In addition, potential interactions between this retarder and a FLA composed of AMPS[®] and N,N-dimethyl acrylamide (CaAMPS[®]-*co*-NNDMA) in cement slurry

were studied. Here, the aim was to find out whether the performance of one additive was influenced by the other, or whether there was any incompatibility.

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 10 A was used.¹⁴ Its clinker composition was determined through quantitative powder XRD technique using Rietveld refinement. The results are displayed in Table I. The amounts of gypsum (CaSO₄·2H₂O) and of hemi-hydrate (CaSO₄·0.5H₂O) present in the cement sample were measured by thermogravimetry. Free lime (CaO) was quantified using the extraction method established by Franke.¹⁵ According to the method developed by Blaine, the specific surface area of cement was found at 3058 cm²/g. The specific density of this sample was 3.18 kg/L, as measured by Helium pycnometry. Particle size distribution of the cement sample was determined employing a laser-based particle size analyzer, which produced a d_{50} value of 11 μm (see 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 1857 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.

CaAMPS[®]-*co*-itaconic acid retarder

The copolymer of AMPS[®] and itaconic acid was synthesized by aqueous free radical copolymerization. The molar ratio between AMPS[®] and itaconic acid

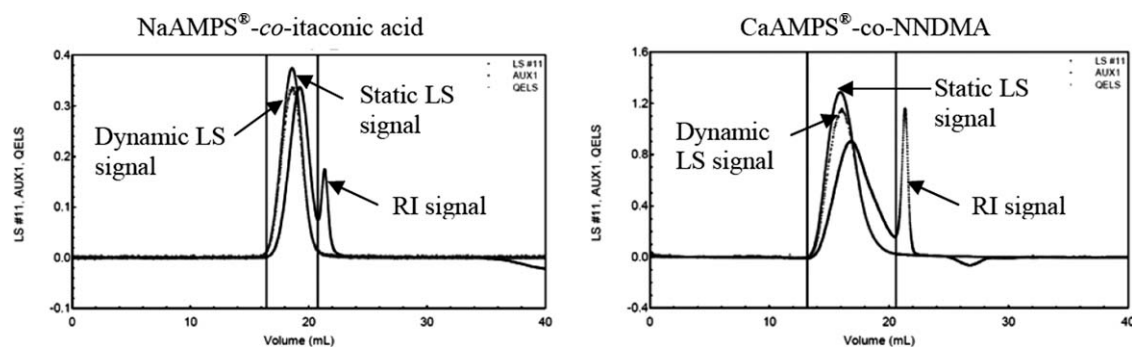


Figure 1 GPC diagrams of NaAMPS[®]-*co*-itaconic acid retarder (left) and CaAMPS[®]-*co*-NNDMA fluid loss additive (right); eluent: 0.2M NaNO₃, pH = 9.

employed was 1 : 0.41. Laboratory grade AMPS[®] (Type 2402, Lubrizol, Wickliffe, OH; AMPS[®] is a registered trademark of the Lubrizol company) and itaconic acid (Acros Organics, Geel, Belgium) were used. In a five-necked, 2 L round-bottom flask, the AMPS[®] monomer was dissolved stepwise in degassed, distilled water to produce a 33 wt % solution. While dissolving the monomer, the pH was adjusted to 10 using 50 wt % aqueous NaOH. Next, solid itaconic acid was added to the solution over a period of 15 min. After heating to 55°C, 2% by weight of the monomers of sodium persulfate initiator were added to the reaction mixture. The reaction flask was heated further to 80°C and kept at this temperature for 3 h under constant stirring. The resulting viscous, yellowish copolymer solution had a solid content of 37 wt %. The copolymer solution was then dialyzed for one day using a Spectra/Por[®] dialysis membrane (MWCO 15,000; Spectrum Laboratories, Rancho Dominguez, CA) to remove any unreacted monomers and salts. Purity of the copolymer was evidenced in the gel permeation chromatography, which confirmed the absence of monomers and salts (see Fig. 1). GPC analysis produced molar masses for the retarder of $\sim 1.8 \times 10^5$ g/mol (M_w) and 1.1×10^5 g/mol (M_n), respectively. Those and other characteristic properties of the copolymer are displayed in Table II. Molar composition of the copolymer was checked by ¹H NMR spectroscopy (Fig. 2). Based on the integrals of methylene protons present in the monomers AMPS[®] and itaconic acid,

a molar ratio of 1 : 0.32 was found. This value deviates from the ratio of monomers added and is owed to the higher reactivity of AMPS[®]. According to the *Q-e* values for both monomers, AMPS[®] polymerizes faster than itaconic acid.¹⁶ The chemical structure of NaAMPS[®]-*co*-itaconic acid is shown in Figure 3.

CaAMPS[®]-*co*-NNDMA fluid loss polymer

The copolymer of AMPS[®] and *N,N*-dimethyl acrylamide (molar ratio of monomers = 1 : 0.63) was synthesized using the aqueous free radical copolymerization method described in previous work.^{10,11} Laboratory grade AMPS[®] (Type 2402, Lubrizol, Wickliffe, OH) and NNDMA (Sigma-Aldrich Chemical, Munich, Germany) were used. The resulting viscous, slightly yellow 17 wt % aqueous copolymer solution was drum dried at 120°C, yielding a white powder. Figure 3 shows the chemical structure of AMPS[®]-*co*-NNDMA. GPC analysis (see Fig. 1) produced molar masses of $\sim 1.7 \times 10^6$ g/mol (M_w) and $\sim 1.1 \times 10^6$ g/mol (M_n). No unreacted monomers or salts were detected. Further characteristic properties of the FLA are presented in Table II.

INSTRUMENTS AND PROCEDURES

Cement characterization

Phase composition of the cement sample was obtained by X-ray powder diffraction using a Bruker

TABLE II
Molar Masses (M_w , M_n), Polydispersity Index (PDI), Hydrodynamic Radius [$R_{h(z)}$], Radius of Gyration [$R_{g(z)}$], and Anionic Charge Amount in Cement Pore Solution of the AMPS[®]-*co*-Itaconic Acid Retarder and of AMPS[®]-*co*-NNDMA Fluid Loss Additive

Polymer	M_w (Da)	M_n (Da)	PDI (M_w/M_n)	$R_{g(z)}$ (nm)	$R_{h(z)}$ (nm)	Anionic charge amount (C/g)
AMPS [®] - <i>co</i> -itaconic acid retarder	1.8×10^5	1.1×10^5	1.6	n.m. ^a	3	-528
AMPS [®] - <i>co</i> -NNDMA FLA	1.1×10^6	4.9×10^5	2.3	108	29	-360

^a n.m. = not measurable.

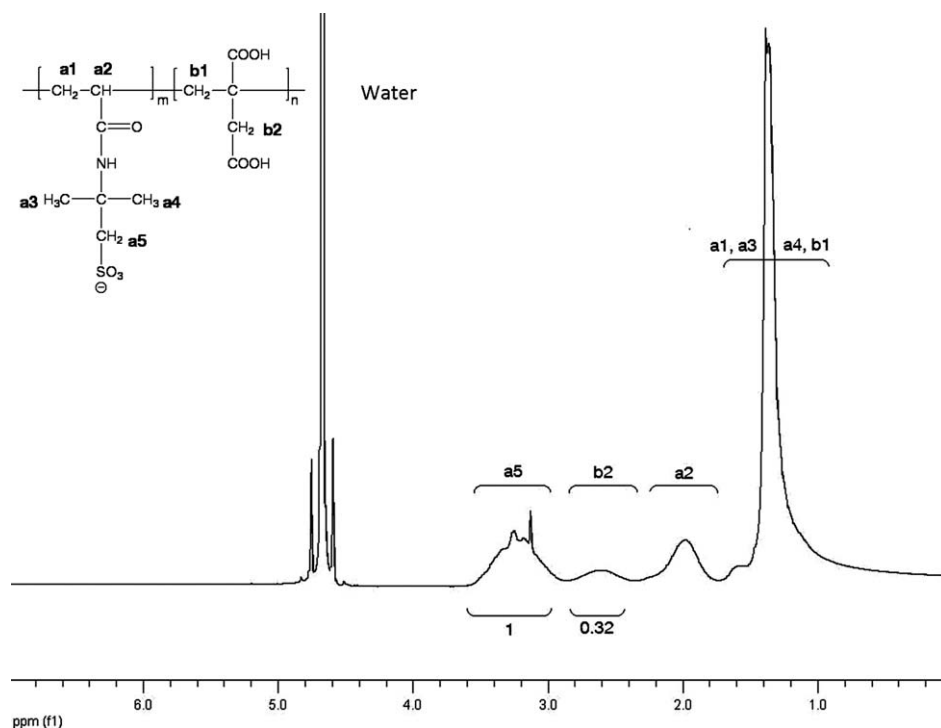


Figure 2 ^1H NMR spectrum of NaAMPS[®]-*co*-itaconic acid retarder after purification by dialysis, measured in D_2O .

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.¹⁷ The instrument was equipped with a scintillation detector using $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation with a scanning range between 5° and $80^\circ 2\theta$. Specific density of the cement sample was measured on an Ultracycrometer[®] 1000 (Quantachrome Instruments, Boynton Beach, FL). The 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).

Polymer characterization

Solids contents of the aqueous polymer solutions were determined using an infrared drying balance (MA35 from Sartorius AG, Göttingen, Germany). Drying conditions were 10 min at 110°C . The values presented are the averages obtained from three separate measurements.

Size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn, Germany) equipped with RI detector 2414 (Waters, Eschborn, Germany)

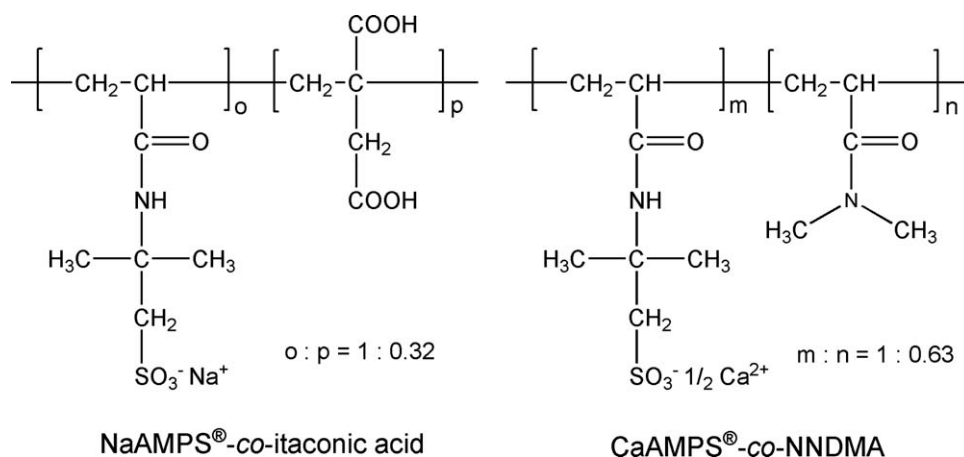


Figure 3 Chemical structures of synthesized NaAMPS[®]-*co*-itaconic acid and of CaAMPS[®]-*co*-NNDMA.

and an 18 angle dynamic light scattering detector (Dawn EOS from Wyatt Technologies, Santa Barbara, CA) was used. The polymers 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 polymer radii [$R_{h(z)}$ and $R_{g(z)}$] were determined using 0.2M aqueous NaNO_3 solution (adjusted to pH 9.0 with NaOH) as eluant at a flow rate of 1.0 mL/min. The value of dn/dc used to calculate M_w and M_n was 0.156 mL/g (value for polyacrylamide).¹⁸

A ^1H NMR spectrum of the synthesized and purified retarder was obtained using a JOEL JMX-GX-270 spectrometer (JOEL GmbH, Eching bei München, Germany) with multinuclear probe. The spectrum was referenced internally to the used solvent deuterium oxide (Merck KGaA, Darmstadt, Germany).

Specific anionic charge amounts of the polymers were determined in DI water or aqueous 0.1M NaOH (pH = 12.6) as a function of the calcium concentration (Ca^{2+} stepwise dosed as solid $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) using a PCD 03 pH apparatus (BTG Mütek GmbH, Herrsching, Germany). Charge titration was carried out according to a literature description employing a 0.001N solution of laboratory grade poly(diallyl dimethyl ammonium chloride) from BTG Mütek GmbH, Herrsching, Germany as cationic polyelectrolyte.¹⁹ The values presented in this study are the average obtained from three different measurements. The deviation of this method was found to be ± 5 C/g.

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 API.²⁰ The slurries were mixed at a water-to-cement (w/c) ratio of 0.44 using a blade-type laboratory blender manufactured by Waring Products (Torrington, CT). Admixture dosages are stated in percent by weight of cement (bwoc). In all experiments conducted at 150°C and higher, 35% bwoc of microsilica were added to the cement slurry to prevent strength retrogression of cement induced by high temperature. Prior to cement addition, the synthesized retarder was dissolved in the mixing water, which was DI water. In contrast to this, the powdered FLA was always dry blended with cement, which within 15 s was added to the mixing water placed in the cup of a Waring blender. There, it was mixed for 35 s at 12,000 rpm. To ensure homogeneous consistency, all slurries were stirred in an atmospheric consistometer (model 1250 from Chandler Engineering, Tulsa, OK) for

20 min at 27 or 80°C, respectively. Pore solution of the neat cement slurry (no polymer present) was produced by vacuum filtration (12 mbar) using a diaphragm vacuum pump (Vacuubrand GmbH, Wertheim, Germany).

Cement slurry thickening time

The time span during which the cement slurry remained in a pumpable, fluid state was determined using a high temperature, high pressure (HTHP) consistometer (model 8240 from Chandler Engineering, Tulsa, OK). This instrument is capable of measuring the consistency (viscosity) of cement slurries under conditions of high temperature (up to 315°C) and high pressure (up to 2750 bar). Slurry viscosity was 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 slurry as prepared 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. Here, effectiveness of the NaAMPS[®]-*co*-itaconic acid cement retarder was tested at temperatures up to 200°C and 400 bar pressure (heating rate 1.2°C/min; pressure rate 8.9 bar/min). Note: These conditions are extreme and for safety reasons, only well-trained and experienced laboratory personnel are recommended to operate this pressure equipment.

Rheology measurement

For rheological measurements of cement slurries, a Couette-type coaxial cylinder rotational viscometer, FANN 35SA (Fann Instruments Company, Houston, TX) equipped with R1 rotor sleeve (rotor radius: 18.4 mm), B1 bob (radius: 17.3 mm; height: 38.0 mm) and F1 torsion spring was used. The values of the viscometer reading were recorded for 6 speeds of the rotor (3, 6, 100, 200, 300, and 600 rpm). The value of shear stress τ (Pa) was calculated by including the torsion spring factor (N cm/degree), the shear stress constant for the effective bob surface (cm^{-3}), and the shear rate constant (s^{-1}/rpm).²⁰

Fluid loss test

Static fluid loss was measured at 80°C using a 500 mL HTHP stainless steel filter press 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.²⁰ After pouring the homogenized slurry obtained from the atmospheric consistometer into the HTHP cell, a heating jacket (OFI Testing Equipment, Houston, TX) 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 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.²⁰ The values reported for the respective API fluid loss test represents the average obtained from three separate measurements. The maximum deviation of the fluid loss value was ± 10 mL/30 min.

Polymer adsorption

Adsorbed amounts of the polymers were determined from the filtrate collected by vacuum filtration. Generally, the depletion method was applied, that is, it was assumed that the decrease in the polymer concentration before and after contact with cement solely resulted from adsorption on the mineral surface. This assumption was confirmed through a solubility test. For this purpose, 45.6 g/L of individual polymer (this concentration correlates to a polymer dosage of 2.0% bwoc) were dissolved in cement pore solution and stored for one day. No precipitation of polymer was observed, thus confirming that depletion resulted from adsorption of the polymer. Achievement of adsorption equilibrium was confirmed by zeta potential values, which were constant at the time of collecting the filtrate for adsorption measurement. The adsorbed amount was calculated from the difference in the equilibrium concentration of the polymer present in the liquid phase before and after adsorption (depletion method). When NaAMPS[®]-*co*-itaconic acid was the sole polymer present in the cement filtrate, a High TOC II apparatus (Elementar, Hanau, Germany) equipped with a CO₂ detector was used to quantify polymer adsorption. Before conducting the TOC analysis, the alkaline cement filtrate containing the unadsorbed polymer was adjusted to pH 1.0 by adding 0.1M HCl.

In the binary additive system, adsorbed amounts were determined from the filtrate collected in the respective fluid loss test. The amount of FLA adsorbed on cement was determined at 80°C by viscosity measurements using an Ubbelohde viscometer (501-10/I, 501-20/II capillaries from Schott Instruments, Mainz, Germany). CaAMPS[®]-*co*-NNDMA increases the viscosity of the filtrate substantially whereas the retarder does not. Using the calibration curve shown in Figure 4, the FLA concentration present in the filtrate was calculated. Knowing the adsorbed amount

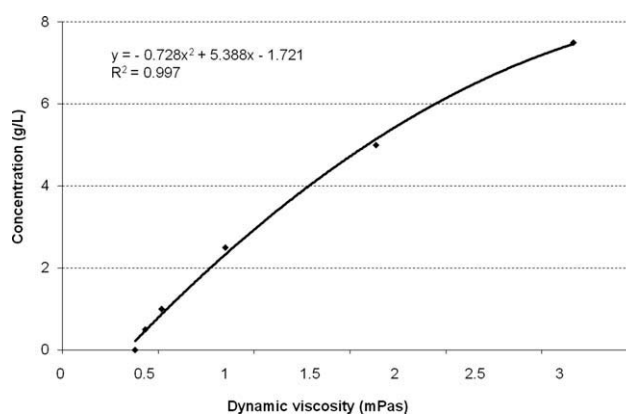


Figure 4 Calibration curve used to determine the concentration of CaAMPS[®]-*co*-NNDMA as derived from dynamic viscosity data of the polymer dissolved in cement pore solution, measured at 80°C.

of the FLA, adsorption of the NaAMPS[®]-*co*-itaconic acid retarder can be calculated from the TOC data by subtracting from the total organic carbon content the carbon content originating from the FLA. The balance in carbon content was then converted into concentration of nonadsorbed retarder.

Zeta potential measurement

Zeta potential of cement slurries was measured at room temperature on an electro acoustic spectrometer (DT-1200 from Dispersion Technology, Bedford Hills, NY).²¹ Since zeta potential was determined as a function of time (here 30 min), 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 ± 1 mV.

RESULTS AND DISCUSSION

Performance of NaAMPS[®]-*co*-itaconic acid

To quantify the effectiveness of the retarder, temperature-dependent thickening times (period until the cement slurry reaches a consistency of 70 Bc) of cement slurries containing 1.0% bwoc NaAMPS[®]-itaconic acid copolymer were measured at temperatures up to 200°C (Table III). At room temperature and 100°C respectively, the slurry remains pumpable over a period of 8 h. Raising the temperature to 150°C reduces the thickening time to about 3 h and at 200°C, a thickening time of 1 h and 15 min only was reached. Such period is much too short for practical field use, which requires a thickening time of at least 4 h.

To study the performance of this retarder under the extreme conditions of 200°C and 400 bar, dosage dependent thickening times were developed.

TABLE III
Thickening Times of Cement Slurries Holding 1.0% bwoc of NaAMPS[®]-*co*-Itaconic Acid Retarder, Measured at Different Temperatures and 400 Bar Pressure

Temperature (°C)	Thickening Time (h : min)
27	>8 : 00
100	>8 : 00
150 ^a	2 : 58
200 ^a	1 : 15

^a Thirty-five percent bwoc of silica flour were added to these cement slurries to prevent cement strength retrogression.

According to the data presented in Table IV it is possible to achieve a thickening time of more than 4 h by employing a dosage of this retarder of 2% bwoc. The result demonstrates that this copolymer has excellent retarding capability even under the extreme condition of 200°C.

Of practical relevance is the potential effect of retarders on cement slurry rheology. This property was tested by adding different dosages of NaAMPS[®]-*co*-itaconic acid to cement slurries. The data obtained are presented in Table V. At a dosage of only 0.1% bwoc of NaAMPS[®]-*co*-itaconic acid, cement slurry rheology already dropped, compared to the neat cement system. Further increase of the retarder dosage ($\geq 0.2\%$ bwoc) causes thinning and even sedimentation (so-called "bleeding") of the slurry, as was evidenced by a rapidly increasing free water content (Table V). Apparently, this retarder possesses strong dispersing ability on cement. Such secondary effect must be considered when formulating cementing systems for field use. In consequence, it means that this copolymer is most suitable for high-density cement slurries possessing low *w/c* ratios, which are prevalent at high temperatures anyway.

Working mechanism of the retarder

To understand the retarding effect of the NaAMPS[®]-*co*-itaconic acid copolymer, a series of experiments was conducted. First, the anionic charge amount of the

TABLE IV
Thickening Times of Cement Slurries (*w/c* = 0.44, 35% bwoc of Microsilica) Holding Different Dosages of NaAMPS[®]-*co*-Itaconic Acid Retarder, Measured at 200°C and 400 bar

Retarder Dosage (% bwoc)	Thickening Time (h : min)
1.0	1 : 15
1.2	1 : 56
1.4	2 : 32
1.6	3 : 35
1.8	3 : 55
2.0	4 : 11

retarder was determined by charge titration using a cationic polyelectrolyte. The results are displayed in Figure 5. At pH = 7, the anionic charge of the NaAMPS[®]-*co*-itaconic acid copolymer is independent of the Ca²⁺ concentration and attains a value of ~ -450 C/g. Apparently, at this pH value most of the carboxylic groups are still protonated and the anionic charge is mostly owed to the sulfonate groups present in NaAMPS[®]-*co*-itaconic acid. Sulfonate groups, however, are not subject to chelation by calcium ions. At the increased pH of 12.8 the carboxylic groups of the copolymer are mostly deprotonated, as is evidenced by a significantly higher anionic charge (~ -650 C/g). Addition of increased dosages of Ca²⁺ ions to this solution, however, decreases the anionic charge amount of the polymer to a final value of ~ -400 C/g. This value is obtained at a calcium concentration of ~ 0.5 g/L and marks the saturation point for the uptake of Ca²⁺ by the carboxylate groups. According to this result, 1 g of NaAMPS[®]-*co*-itaconic acid retarder can chelate ~ 5 g of Ca²⁺ ions, thus indicating strong calcium binding capacity. This value is 46 times higher than the stoichiometric amount, assuming that each carboxylate group present in the copolymer chelates one Ca²⁺ ion. Based on this result, it can be concluded that for the enormous calcium binding capability of this retarder not only the electrostatic attraction of Ca²⁺ by anionic functionalities present in the polymer plays a role, but also the coordination to various donor atoms contained in

TABLE V
Shear Rate Dependent Rheology (Shear Stress) and Free Water Content of Cement Slurries Containing Different Dosages of NaAMPS[®]-*co*-Itaconic Acid Retarder, Measured at 27°C

Retarder dosage (% bwoc)	Shear stress (mPa) at different shear rates (s ⁻¹)						Free water content (mL)
	1022	511	340	170	10.2	5.1	
0	56	80	94	138	1281	2028	–
0.1	51	66	80	125	907	1174	4
0.2	30	28	29	29	53	107	7
0.3	27	24	26	26	53	107	19
0.4	28	24	26	22	53	107	114

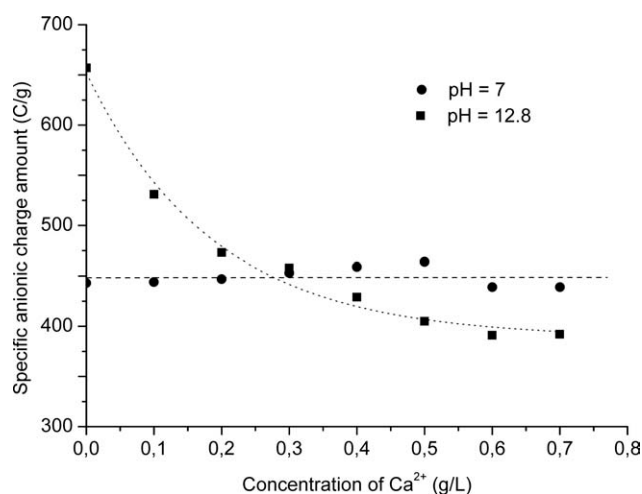


Figure 5 Specific anionic charge amount of NaAMPS[®]-*co*-itaconic acid ($c_{\text{polymer}} = 0.1$ g/L) as a function of Ca²⁺ concentration, measured at pH = 7 and 12.8, respectively.

the retarder molecule. A similar observation has been made before for lignosulfonate retarder, which exhibits a calcium binding capacity of 1 g Ca²⁺ per gram.²² In comparison, the CaAMPS[®]-*co*-NNDMA fluid loss polymer, which does not retard cement possesses a calcium binding capacity of < 0.01 g calcium per gram copolymer only. Obviously, this extraordinarily high calcium binding capacity plays a key role for the retarding efficacy of the AMPS[®]-itaconic acid copolymer.

Next, a potential contribution of adsorption to the retarding performance was considered and probed by measuring the amount of polymer adsorbed on cement and the zeta potential of cement slurries treated with the polymer. If NaAMPS[®]-*co*-itaconic acid does indeed adsorb on cement, then its adsorbed amount should increase linearly with dosage until a plateau is reached, which represents coverage of the cement surface with the maximum possible amount of polymer. This behavior is best represented by a Langmuir type isotherm. The results obtained are displayed in Figure 6. There, it is shown that the adsorbed amount in fact increases linearly and rapidly with polymer dosage until it reaches a value of saturation, which lies at 1.5 mg polymer/g cement and is obtained at a polymer dosage of 0.2% bwoc. At higher retarder dosages, the adsorbed amount remains constant.

Polymer adsorption also was confirmed via zeta potential measurement of cement slurry containing increased copolymer dosages. The data obtained are presented in Figure 7. When polymer dosage is increased, the zeta potential decreases from -5.9 mV for the neat cement slurry to -24.8 mV at a retarder dosage of 0.2% bwoc. Addition of more retarder results in no further change of the zeta potential, proving that saturated adsorption has occurred at

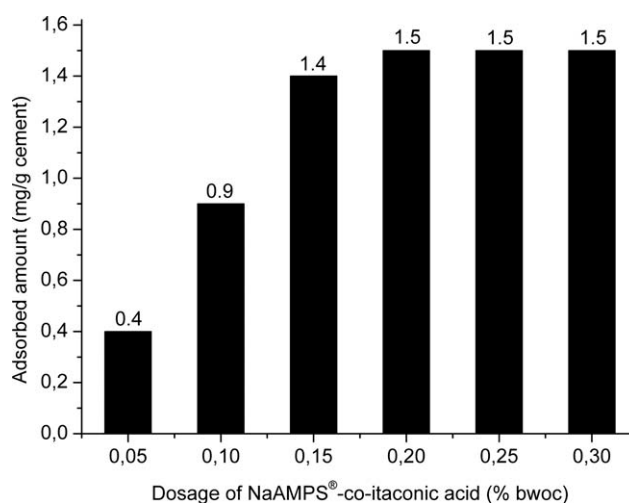


Figure 6 Dosage dependent adsorbed amount of NaAMPS[®]-*co*-itaconic acid on oil well cement, measured at 27°C.

this polymer concentration. Thus, it is demonstrated that a negatively charged layer of polymer is deposited onto the hydrating cement particles. Nevertheless, this layer seems to be permeable for water molecules and it has no effect on cement hydration, as will be shown later. The zeta potential results also explain the dispersive effect of the retarder. Through adsorption, the cement particles are loaded with anionic polymer and become highly negatively charged. As a result electrostatic repulsion between the cement particles occurs.

Interaction with CaAMPS[®]-*co*-NNDMA FLA

Between different additives present in oil well cement, multiple interactions are possible, as has been shown in previous work.^{10,11,12,22} Here, as the

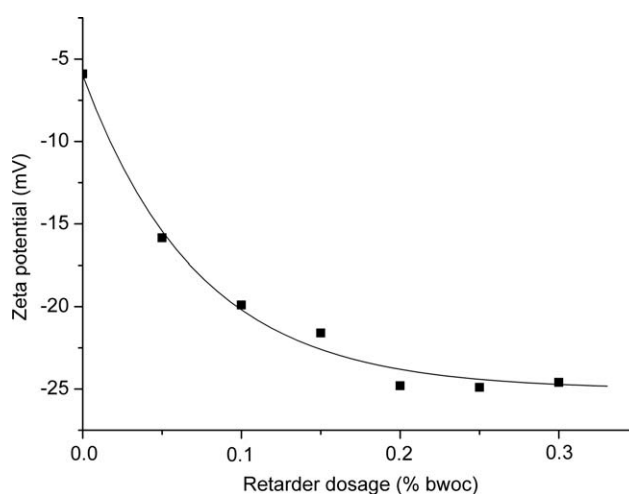


Figure 7 Zeta potential of API Class G oil well cement slurry ($w/c = 0.44$) holding increased dosages of NaAMPS[®]-*co*-itaconic acid retarder, measured at 27°C.

TABLE VI
API Fluid Loss and Thickening Time of Cement Slurries Containing Different
Amounts of CaAMPS[®]-*co*-NNDMA and NaAMPS[®]-*co*-Itaconic Acid,
Measured at 80°C

CaAMPS [®] - <i>co</i> -NNDMA fluid loss additive (% bwoc)	NaAMPS [®] - <i>co</i> -itaconic acid retarder (% bwoc)	API fluid loss (mL)	Thickening Time (h : min)
0.5	-	100	1 : 47
0.5	0.1	136	3 : 20
0.6	0.1	106	3 : 19
0.7	0.1	82	3 : 21
0.8	0.1	76	3 : 20

working mechanism of the NaAMPS[®]-itaconic acid retarder is based on adsorption, the potential exists that it will perturb the effectiveness of other additives, which also work by adsorption. The reason behind is competition for a limited number of adsorption sites on the surface of cement. A potential candidate for such undesired interaction is the fluid loss control agent CaAMPS[®]-*co*-NNDMA, which also relies on adsorption.^{10,11} To evaluate, performance of this FLA was tested at 80°C in absence and presence of the retarder. The results are displayed in Table VI.

There it is evident that at a FLA dosage of 0.5% bwoc, addition of only 0.1% bwoc of the NaAMPS[®]-itaconic acid copolymer increases API fluid loss from 100 to 136 mL. Obviously, owed to the high anionic charge amount of the retarder (-528 C/g) and its small steric size ($R_{h(z)} = 3$ nm), the FLA (anionic charge amount -360 C/g, $R_{h(z)} = 29$ nm) is partially displaced from the surface of cement hydrates. The negative effect of the retarder on cement fluid loss can be corrected by increasing the dosage of CaAMPS[®]-*co*-NNDMA by 20 to 0.6% bwoc. This result instigates that CaAMPS[®]-*co*-NNDMA competes with NaAMPS[®]-*co*-itaconic acid for the limited number of adsorption sites existing on the surface of cement.

To further probe into the competitive adsorptive mechanism between the two copolymers, the adsorbed amounts of CaAMPS[®]-*co*-NNDMA and of NaAMPS[®]-*co*-itaconic acid were quantified individually via viscosity measurement and TOC analysis of HTHP filtrates obtained at 80°C (Fig. 8). When 0.1% bwoc of retarder were dosed to the cement slurry containing 0.5% bwoc of the FLA, the adsorbed amount of CaAMPS[®]-*co*-NNDMA decreased from 4.8 mg polymer/g cement (this value corresponds to 96% of FLA dosage added) to 4.3 mg polymer/g cement (corresponding to 86% of dosage added). From the retarder, 0.7 mg/g cement, or 60% of dosage added, are adsorbed and occupy surface sites between the larger FLA molecules. Apparently, the NaAMPS[®]-itaconic acid copolymer takes some of the

adsorption sites and hence adsorption of CaAMPS[®]-*co*-NNDMA and its effectiveness regarding fluid loss control are decreased. When FLA dosage is increased further to 0.8% bwoc, then its adsorbed amount rises to 6.8 mg polymer/g cement (this value corresponds to $\sim 87\%$ of FLA dosage added). In the presence of 0.1% bwoc of retarder, always $\sim 87\%$ of FLA dosage added adsorb, independent of FLA concentration. As the adsorbed amount of FLA increases, the adsorbed amount of NaAMPS[®]-*co*-itaconic acid decreases continuously from 0.7 mg/g cement (FLA dosage: 0.5% bwoc) to 0.4 mg/g cement (FLA dosage: 0.8% bwoc). As a result, adsorption of the retarder expressed as percentage of dosage added decreases from 60 to 40%. Obviously, an inverse correlation between the adsorbed amounts of the two polymers exists. The result indicates that in the equilibrium state, the adsorbed amount of retarder adjusts to the amount of FLA

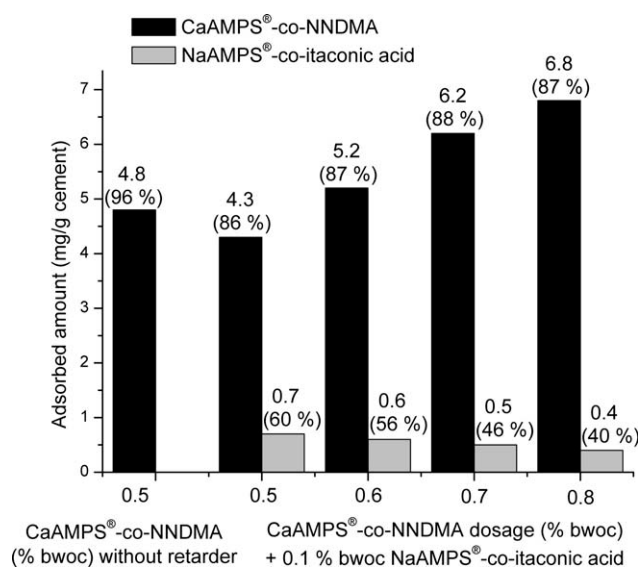


Figure 8 Adsorbed amounts of CaAMPS[®]-*co*-NNDMA and NaAMPS[®]-*co*-itaconic acid on oil well cement, measured at 80°C in slurries containing different dosages of FLA and 0.1% bwoc retarder; () = adsorbed amounts in percentage of dosage added.

polymer adsorbed, which apparently has a higher tendency to occupy the surface of cement. Nevertheless, in spite of the decreased adsorbed amount, the retarding effectiveness of the copolymer is not affected, as is evidenced in Table VI. This instigates that for this retarder, adsorption onto cement plays no role in the retarding efficacy. The working mechanism of NaAMPS[®]-*co*-itaconic acid solely relies on its enormous calcium binding capacity.

Consequently, for every binary system containing both polymers it is difficult to predict, which additive will adsorb preferentially and which one will be able to develop its full capacity and vice versa. This effect has to be considered when combining NaAMPS[®]-*co*-itaconic acid set retarder with other admixtures such as CaAMPS[®]-*co*-NNDMA FLA.

CONCLUSION

At high temperatures, the synthesized NaAMPS[®]-itaconic acid copolymer shows excellent retardation of oil well cement. In addition, the copolymer exhibits a significant dispersing effect on cement.

The working mechanism of the NaAMPS[®]-*co*-itaconic acid retarder exclusively relies on its huge calcium binding capacity. Chelation of calcium ions dissolved in the cement pore solution by carboxylate groups and donor atoms present in the retarder hinders the formation and early growth of seed crystals of cement hydrates, as less calcium is available for their growth. This mechanism is unusual because it relies on one effect only, whereas common cement retarders work by a combination of different effects, for example adsorption and calcium complexation.^{2,4} Obviously, the fact that NaAMPS[®]-*co*-itaconic acid still is such a powerful retarder is owed to its exceptionally high calcium binding capacity, which significantly exceeds that of other common cement retarders. Still, a part of the polymer adsorbs on cement, but this effect does not contribute to the retarding efficacy of the copolymer.

Because of its high anionic character, NaAMPS[®]-*co*-itaconic acid may perturb adsorption of other anionic additives and thus negatively affect their performance. Here, it was shown that this retarder

could reduce the effectiveness of CaAMPS[®]-*co*-NNDMA FLA by decreasing its adsorbed amount. Such negative interaction has to be taken into account when formulating more complex admixture systems.

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