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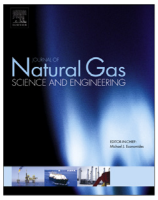

Synthesis, characterization and performance of a novel phosphate-modified fluid loss additive useful in oil well cementing

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ABSTRACT

A phosphate-modified terpolymer comprising of 2-acrylamido-2-tert-butyl sulfonic acid (ATBS), N,N-dimethyl acrylamide (NNDMA) and 2-(methacryloxy)ethyl phosphate (MEP) was synthesized by aqueous free radical copolymerization and evaluated as fluid loss additive (FLA) in oil well cement. Successful incorporation of MEP was confirmed *via* ^{1}H NMR spectroscopy, and molecular properties of the terpolymer were determined using size exclusion chromatography. It was found that the presence of phosphate anchor groups along the polymer backbone enhances the FLA's performance in cement slurries at high temperatures (up to 140 °C) and in sea water when compared with commonly used ATBS-co-NNDMA or its counterpart composed of ATBS, NNDMA and 2-(methacryloxy)ethanol which bears a hydroxyl instead of the phosphate functionality. The phosphate-modified FLA also revealed better effectiveness and robustness when combined with acetone–formaldehyde–sulfite (AFS) dispersant or ATBS-co-acrylic acid retarder. Adsorption measurements suggest that the superior fluid loss performance is owed to higher adsorption of the phosphated FLA. Measurements of the adsorbed layer thickness on cationic polystyrene particles indicate that the phosphated FLA adsorbs in a train-like conformation which results from the strong affinity of the phosphate anchor groups to the positively charged surface.

1. Introduction

In oil and gas well cementing, steel pipes (casings) are placed into the borehole, and then the annular space between the casing and the borehole is sealed with a cement slurry in order to stabilize the borehole, keep the casing in place, prevent corrosion of the casing resulting from salt brine influxes and, most important, to avoid the migration of fluids upwards or downwards in the borehole to other formations ("zonal isolation") (Smith, 1990). To achieve this, the properties of the oil well cement slurry are tailored to the conditions existing in the wellbore through the addition of additives. For example, dispersants and retarders are employed to reduce the viscosity of the cement slurry and to delay its setting or thickening time, thus allowing pumpability over a distance of several kilometres. Furthermore, fluid loss additives (FLAs) are added to reduce uncontrolled water loss from the slurry while being pumped along a porous formation (Nelson and Guillot, 2006; Fink, 2003).

At higher temperatures, a synthetic FLA copolymer composed of the monomers 2-acrylamido-2-tert-butyl sulfonic acid (ATBS) and N,N-dimethyl acrylamide (NNDMA) is frequently applied. This anionic ATBS-co-NNDMA polymer provides fluid loss control by reducing filter cake permeability through polymer adsorption onto the positively charged surfaces of cement hydration products (adsorptive working mechanism) (Plank et al., 2006; Desbrieres, 1993). However, when highly anionic dispersants such as acetone-formaldehyde-sulfite (AFS) polycondensate or retarders including 2-acrylamido-2-tert-butyl sulfonic acid -co- acrylic acid (ATBS-AA copolymer) are present in the cement slurry, then adsorption, and thus functionality, of the ATBS-co-NNDMA FLA which possess medium anionicity only is severely impeded. In its place, AFS or ATBS-co-AA occupy the surfaces of cement hydrates whereas most of the FLA copolymer remains dissolved in solution. Consequently, such competition for adsorption sites results in poor fluid loss control of the cement slurry which can lead to incomplete cement hydration and thus insufficient sealing of the borehole (Plank et al., 2009, 2013).

One approach to overcome the problem of reduced effectiveness of the FLA is to synthesize the ATBS-co-NNDMA copolymer by using the so called MADIX (= Macromolecular Design by the Interchange

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of Xanthates) method (Cadix et al., 2015). There, the copolymerization of ATBS and NNDMA is controlled by xanthates in order to produce diblock instead of alternating copolymers. This modification introduces strongly adsorbing blocks of sulfonate groups into the FLA which greatly enhance its adsorption and thus its effectiveness in the presence of other highly anionic additives such as AFS. However, this synthesis method is protected by a patent and also may result in a fluid loss polymer with lower molecular weight which decreases its performance at higher temperatures (Wilson et al., 2016).

Alternatively, the ATBS-co-NNDMA polymer can be modified with stronger anchor groups. For example, in previous works ATBS and NNDMA were copolymerized with vinyl phosphonic acid or maleic anhydride as additional comonomers resulting in ATBS-based FLAs with significantly enhanced adsorption and performance (Plank et al., 2007). So far, however, phosphate groups which exhibit a significantly stronger Ca^{2+} complexation potential than phosphonate, carboxylate or sulfonate groups (Amjad, 1987) have not yet been studied as potential candidates to improve the adsorption and thus the performance of synthetic FLAs.

For this purpose, a common ATBS-co-NNDMA FLA was modified with 2-(methacryloxy)ethyl phosphate (MEP) as comonomer in order to introduce a phosphate anchor group. The resulting ATBS-co-NNDMA-co-MEP terpolymer was characterized and probed with respect to its compatibility with AFS and ATBS-co-AA, respectively, and its temperature stability and performance in sea water based cement slurries was compared with that of commonly used ATBS-co-NNDMA and of ATBS-co-NNDMA-co-ME (ME = 2-(methacryloxy)ethanol) terpolymer which contains hydroxyl instead of phosphate groups. This comparison allowed to assess the effect of the phosphate anchor on the performance of the FLA. Furthermore, to elucidate the mechanism of action, adsorption of each individual admixture and of combinations were determined. Lastly, the adsorbed layer thickness of the FLAs on cationic polystyrene nanoparticles was measured *via* dynamic light scattering (DLS) to assess the influence of the phosphate anchor group on the adsorbed conformation and hence on the ability of the FLA to constrict the pores in the cement filter cake and to reduce fluid loss from cement.

2. Experimental

2.1. Materials

2.1.1. Oil well cement

An oil well cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) corresponding to specification 10 A of the American Petroleum Institute (API) was used for this study (American Petroleum Institute, 2010). Its clinker composition was investigated *via* quantitative powder X-ray diffraction technique with *Rietveld* refinement (McCusker et al., 1999). The free lime (CaO) content was assessed using the extraction method according to *Franke* (Franke, 1941). The amounts of hemi-hydrate ($CaSO_4 \cdot 0.5H_2O$) and of gypsum ($CaSO_4 \cdot 2H_2O$) were determined by thermogravimetry while particle size distribution was evaluated employing laser granulometry. There, a d_{50} value of 11.0 μm was obtained. Density (3.18 kg/L) was measured by helium pycnometry and the value for the surface area (3058 cm^2/g) was captured by the *Blaine* method. The results are summarized in Table 1.

2.1.2. Chemicals

2-Acrylamido-2-tert-butyl sulfonic acid (ATBS; AMPS® 2404 monomer; > 99% purity) was received from Lubrizol (Rouen, France). AMPS® is a registered trademark of the Lubrizol Corporation (Wickliffe, Ohio). Tetraethylene pentamine (purity 95%), sodium hydroxide (> 98%) and sodium peroxodisulfate (> 99%) were purchased from Merck (Darmstadt, Germany), while N,N-dimethylacrylamide (NNDMA; purity > 99%) and 2-(methacryloxy)ethanol (ME, > 99%) are acquired from Sigma-Aldrich (Munich, Germany). 2-(Methacryloxy)ethyl phosphate (MEP, purity > 91%) was obtained from Polyscience Europe GmbH (Hirschberg, Germany). Deionized water (DI water) purified by a Nanopure Diamond water purification system (Thermo Scientific, Waltham, USA) was used in all experiments.

2.1.3. Synthesis and characterization of the FLAs

First, the Ca^{2+} salt of NNDMA and ATBS was prepared as reference FLA (CaATBS-co-NNDMA) following the description in a previous work (Plank et al., 2006). Furthermore, terpolymers of ATBS and NNDMA with either 2-(methacryloxy)ethyl phosphate (MEP) or 2-(methacryloxy)ethanol (ME) were synthesized by the same method. However, the process was slightly varied as the polymerization was performed in the presence of Na^+ ions to avoid precipitation of the phosphate monomer with Ca^{2+} ions. In a typical preparation, 82.0 g (0.40 mol, 1.00 Eq.) of ATBS were dissolved in 680 mL of a degassed, 2.4 wt. % aqueous sodium hydroxide solution. This monomer solution has to be kept at all times at pH > 7 and a temperature < 25 °C to avoid homopolymerization. Next, 24.1 g NNDMA (0.24 mol, 0.63 Eq.) and 2.5 g MEP (0.01 mol, 0.03 Eq.) or 1.6 g ME (0.01 mol, 0.03 Eq.) were added, whereby the pH of the combined monomer solution was adjusted to pH = 9.5 through the addition of a 7.5 M sodium hydroxide solution. Then the temperature was raised to 60 °C and 0.8 g aqueous tetraethylene pentamine solution (21.8 wt. %, 0.90 mmol) and sodium peroxodisulfate initiator (1.2 g dissolved in 10 mL DI water) were added to the mixture to initiate polymerization. The temperature of the solution was kept for 2 h at 60 °C while stirring constantly. As a result of polymerization, the reaction mixture became increasingly viscous. In order to avoid a too viscous polymer solution, the reaction mixture was diluted with ~ 20 mL DI water every 5 min within the first 30 min of polymerization. Finally, the solution was cooled to room temperature yielding a viscous, yellowish polymer solution with a solid content of ~ 10 wt. % and a pH value of ~ 7. Chemical structures of the FLAs are illustrated in Fig. 1.

Molecular weights (M_w, M_n), polydispersity Index (PDI) and hydrodynamic radius ($R_{h(z)}$) of the synthesized FLAs were determined by size exclusion chromatography (SEC). There, an aqueous 0.2 M $NaNO_3$ solution (pH = 9) at a flow rate of 1.0 mL/min was applied as an eluant. The FLAs were dissolved in the eluant and filtered through a 5 μm syringe filter (Pall Corporation, Cornwall, UK) prior to the measurement. Separation was performed on a Waters Alliance 2695 separation module equipped with an Aquagel® precolumn and two Aquagel-OH® 60 columns (from Polymer Laboratories, Santa Clara, California). Spectra were recorded with an RI detector (2414 from Waters, Eschborn, Germany) and an 18 angle dynamic light scattering detector (Wyatt Dawn EOS, Santa Barbara, California). For the evaluation of M_w and M_n a value for *dn/dc* of 0.156 mL/g (value for polyacrylamides) was applied (Huglin et al., 1989).

The anionic charge amounts of the FLAs were determined in 0.1 M NaOH and cement pore solution. There, the anionic polymer was titrated with poly(diallyl dimethylammonium chloride) as cationic polyelectrolyte using a Mütek PCD 03 pH apparatus from BTG Instruments GmbH (Herrsching, Germany).

Table 2 illustrates the properties of all three FLAs.

2.1.4. Synthesis and characterization of the AFS dispersant

The AFS dispersant was synthesized and characterized according to *Aignesberger* and *Plank* as it is reported in previous work (Plank et al., 2006). The chemical structure of AFS is presented in Fig. 1, while its characteristic properties are illustrated in Table 2.