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Influence of electrolytes on the performance of a graft copolymer used as fluid loss additive in oil well cement



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ABSTRACT

The influence of electrolytes contained in sea water and 20 wt% NaCl solution on a high temperature fluid loss additive (FLA) for oil well cement was investigated. The FLA was comprised of a humic acid–{sodium 2-acrylamido-2-methylpropane sulfonate-co-N,N-dimethyl acrylamide-co-acrylic acid} graft copolymer which was tested at 27 °C and 150 °C. Its performance was compared with that of an industrial lignite-based copolymer. It was found that seawater, in spite of its relatively low electrolyte content (~3.6 wt%), affects fluid loss performance of the graft copolymer strongly whereas 20% NaCl dissolved in the mixing water exhibit a minor effect only. Mg²⁺ present in sea water was identified as cause for poor admixture performance. Experiments demonstrate that in the highly alkaline environment of cement, Mg²⁺ precipitates as voluminous Mg(OH)₂ which entraps significant amounts of the graft copolymer. Delayed addition of the graft copolymer to the cement slurry presents a mitigation strategy to overcome the negative effect of Mg²⁺ present in sea water.

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1. Introduction

The global oil and gas industry is challenged to increase production in order to meet the rising world energy demand. One key area being explored now are the reservoirs below massive salt formations. Among the most promising candidates are the deep-water areas in the Gulf of Mexico, the North Sea, offshore Brazil, in the North Caspian Sea, and off North and West Africa (Hunter et al., 2010; Sanz and Dasari, 2010; Martins et al., 2012).

Typically, such salt formations are composed of ~96 wt% NaCl (halite) while the remaining ~4 wt% include sylvite (KCl) and various magnesium and/or calcium salts (Heerema, 2009). For example, the Zechstein formation which runs across Europe from UK, Netherlands, Germany, Poland to Ukraine contains a significant amount of magnesium salts, especially bischofite, MgCl₂·6H₂O (Geluk et al., 2007). Such salt formations can vary from salt domes to massive beds with thicknesses up to 1500 m (Barker and Feland, 1994).

Wells constructed in these areas encounter reservoir fluids containing high electrolyte contents from NaCl, CaCl₂, MgCl₂ and MgSO₄, with total salt concentrations as high as 40 wt%. Besides, bottom hole temperatures often range between 80 °C and 120 °C, and in few cases can reach even higher, e.g. to 150 °C (DeBruijn et al., 2008).

Another source for salt contamination of the cement slurry is

the widespread use of sea water as mixing water on offshore wells. Such practice is mainly owed to better economics as transportation of fresh water to an offshore rig can inflict rather high cost.

The challenge for cementing such subsalt and offshore wells is that the chemical admixtures commonly applied to control the properties of the cement slurry have to perform well even when the slurry is loaded with various types and concentrations of electrolytes. However, salt tolerant additives are rare because most admixtures were designed for fresh water slurries, and often perform poorly in saline environment (Whisonant et al., 1988). For example, it is well established that sea water perturbs the effectiveness of most cement admixtures, although its salt content is only slightly higher (~3 wt% to 4 wt%) compared to that of fresh water (~2 wt%). Surprisingly, the reason for the adverse effects of various salts on these admixtures is still mostly unknown. It is thus imperative to investigate and understand the interactions of oil well cement additives with various electrolytes.

Here, as a representative example for oil well cement additives, a humic acid {sodium 2-acrylamido-2-methylpropane sulfonate-co-N,N-dimethyl acrylamide-co-acrylic acid} graft copolymer which presents a dispersing fluid loss additive was tested at 27 °C and 150 °C respectively in cement slurries prepared from fresh water, sea water and 20 wt% NaCl. Moreover, the impact of these electrolytes in general and of specific ions in particular on the functionality and interaction of this graft copolymer with cement was examined. Based on these findings, a simple method to mitigate the negative effect of specific salts is proposed.

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2. Materials and methods

2.1. Oil well cement and silica flour

An API Class G oil well cement corresponding to American Petroleum Institute (API) Specification 10A was used (API, 2010). Its clinker composition is given in Table 1. A commercial sample of silica flour was included into the cementing system to prevent high temperature induced strength retrogression. Average particle size (d_{50} value) of the silica flour was 32.7 μm .

2.2. Chemicals

2-acrylamido-2-methylpropane sulfonic acid (AMPS[®]), N,N-dimethyl acrylamide (NNDMA), acrylic acid (AA), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sodium chloride (NaCl), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium hydrogen carbonate (NaHCO_3), potassium bromide and sodium sulfate (Na_2SO_4) were used as obtained. As humic acid sample, a 14.5 wt% aqueous solution of potassium humate was utilized. The chemical structures of all raw materials used in the synthesis of the graft copolymer are exhibited in Fig. 1.

2.3. Graft copolymer

The humic acid graft copolymer was prepared by grafting 2-acrylamido-2-methylpropane sulfonic acid (AMPS[®]), N,N-dimethyl acrylamide (NNDMA) and acrylic acid (AA) onto a humic acid backbone via aqueous free radical copolymerization using sodium persulfate as initiator following a literature description (Salami and Plank, 2013). This dispersing graft copolymer is composed of 20 wt% humic acid backbone and 80 wt% graft chains. The molar ratio of the monomers in the graft chain was AMPS[®]/NNDMA/AA = 1:0.31:0.03. In preparation, 117 mL of a 14.5 wt% aqueous solution of commercial potassium humate and 160 mL of DI water were placed in a 1 L four-necked flask equipped with stirrer, thermometer and N_2 inlet. The pH of the solution which initially was 9.2 was adjusted to 12 by feeding of 13.5 g of sodium hydroxide pellets into the flask. Next, in this order: 50 g of AMPS[®], 15 g of NNDMA, 1.2 g of acrylic acid, 0.30 g of EDTA and 1 g of defoamer were added to the solution of potassium humate. While stirring, nitrogen gas was bubbled through for 1 h. Then the temperature was increased to 50 °C and the first amount of $\text{Na}_2\text{S}_2\text{O}_8$ initiator (4.0 g) was added. After 50 min of reaction time, the second portion of the initiator (4.0 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 for another hour to complete the reaction. Finally, the liquid was cooled to room temperature, diluted with 300 mL of DI water and the reaction was quenched by addition of 4.8 g of sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$). The resulting graft copolymer solution constitutes a dark brown, viscous and odorless liquid with a solid content of 19 wt% and a pH value of 7. The molecular weights of

the graft copolymer measured via size exclusion chromatography (SEC) were 309,900 g/mol (M_w) and 161,400 g/mol (M_n) with a corresponding polydispersity index (PDI) of 1.9. The proposed chemical structure of the graft copolymer is shown in Fig. 2.

2.4. Industrial graft copolymer

For comparison, a commercial lignite – based graft copolymer was studied. Its synthesis is described in a patent (Huddleston and Williamson, 1991). According to this literature, the graft copolymer contains ~20 wt% of a lignite backbone and ~80 wt% of graft chains composed of AMPS[®] and dimethyl acrylamide (NNDMA). The molecular weights of the lignite graft copolymer obtained from SEC are 394,000 g/mol (M_w) and 265,000 g/mol (M_n) respectively, with a corresponding polydispersity index (PDI) of 1.5.

2.5. Cement retarder

As cement retarder, a combination of a self-synthesized AMPS[®]-itaconic acid copolymer and of a commercial product based on natural 2R,3R-tartaric acid was used. The AMPS[®]-itaconic acid copolymer was prepared at a molar ratio of 1:0.4 via free radical copolymerization according to literature (Rodrigues, 1999) yielding a viscous, yellowish aqueous solution with a solid content of 39 wt% and a pH value of 4. The molecular weights of the copolymer measured via SEC were: $M_w=175,600$ g/mol; $M_n=108,600$ g/mol and PDI (M_w/M_n) = 1.6.

2.6. Synthetic seawater

Sea water prepared according to the American Standard for Testing Materials (ASTM D1141) was used. The composition of this synthetic sea water is given in Table 2. The resulting ion concentrations (mg/L) were: Na^+ 10,900; Mg^{2+} 1300; Ca^{2+} 418; K^+ 403; Cl^- 19,800; SO_4^{2-} 2800; HCO_3^- 152; Br^- 67.

2.7. Cement slurry preparation and testing

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 (API, 2005a). Fresh and salt water cement slurries were prepared using fresh water, sea water and 20% by weight of water (bwow) NaCl as mixing water. At first, cement was dry blended with the silica flour at a weight ratio of 65:35. This blend was mixed with DI water, sea water or 20% NaCl solution at a water-to-cement (w/c) ratio of 0.48 and a water-to-solids (w/s) ratio of 0.31 (solids = cement + silica) using a blade-type laboratory blender. Within 15 s, the cement/silica blend was added to the mixing water placed in the cup of the Waring blender and mixed for 35 s at 12,000 rpm. All dosages of admixtures (FLA, retarder) are stated in % by weight of cement (bwoc). The aqueous solutions of the graft copolymer and of the AMPS[®]-co-itaconic acid retarder were added to the mixing water

Table 1

Phase composition (XRD, Rietveld), specific density, specific surface area (Blaine) and d_{50} value of API class G oil well cement sample.

C_3S (wt%)	C_2S (wt%)	C_3A_c (wt%)	C_4AF (wt%)	Free CaO (wt%)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (wt%)	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (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 ^b	11

C_3S : tricalcium silicate ($\text{Ca}_3(\text{SiO}_4)\text{O}$); C_2S : dicalcium silicate (Ca_2SiO_4); C_3A_c : cubic modification of tricalcium aluminate ($\text{Ca}_9\text{Al}_6\text{O}_{18}$); C_4AF : tetra calcium aluminate ferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$).

^a Measured by thermogravimetry.

^b Measured with Blaine instrument.

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