



Full Length Article

Evaluating the performance of tailor-made water-soluble copolymers for enhanced oil recovery polymer flooding applications

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ARTICLE INFO

Article history:

Received 20 February 2017

Received in revised form 18 April 2017

Accepted 26 April 2017

Available online 4 May 2017

Keywords:

Water-soluble copolymers

Enhanced oil recovery

Polymer flooding

Tailor-made polymers

ABSTRACT

This work evaluated the performance of designed AAm/AAC copolymers with tailor-made properties in polymer flooding applications for enhanced oil recovery (EOR). Displacement tests using unconsolidated sand-packs with simulated real reservoir conditions were performed to evaluate the effectiveness of the designed copolymers during the displacement of heavy oil having a viscosity of 1192 cP. Experimental results demonstrated the superior mobility control functionality of the AAm/AAC copolymers compared to a commercially available EOR polyacrylamide copolymer. Likewise, higher incremental heavy oil recovery was obtained under the same experimental conditions by the AAm/AAC copolymers. This work identified the best performing copolymers and, more significantly, emphasizes the importance of a systematic approach in designing appropriate copolymers for EOR polymer flooding applications.

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1. Introduction

Copolymers of acrylamide (AAm) and acrylic acid (AAc) have been applied in various applications from biomedical and pharmaceutical to flocculation and enhanced oil recovery (EOR) [1]. The recovery of the oil left behind in the reservoir after secondary recovery methods (i.e., waterflooding and gas flooding) is carried out through the application of EOR processes that involve various techniques, such as thermal and non-thermal processes [2,3]. Polymer flooding is one of the most promising non-thermal EOR methods that uses water-soluble polymers in dilute aqueous solutions to improve the efficiency of oil recovery. The addition of polymer to the injected water (i.e., brine) reduces its mobility through porous media, which according to Sydansk [4] is the “primary conformance-improvement benefit of polymer waterflooding”. Mobility reduction takes place through the synergistic effect of the increased viscosity of the injected water and the reduced permeability of the porous media contacted by the polymer. Permeability reduction could be caused by the simultaneous occurrence of polymer adsorption, mechanical entrapment, hydrodynamic retention, and polymer precipitation due to interactions with formation brine [4,5]. Incremental oil recovery due to polymer

flooding is also attributed to the fact that the improvement of the reservoir conformance allows the polymer water-drive, also called “augmented waterflooding”, to contact a larger volume of the reservoir compared to other driving fluids (i.e., water free-polymer) [4,5]. Among water-soluble polymers, AAm/AAC copolymers are by far the most commonly used synthetic polymers for polymer flooding. In view of the economics of oil production and marketing, the complexities of oil recovery, and its importance within the global energy supply and demand, it is critical to design polymers and modify their properties to improve the efficiency of polymer flooding [3].

In order to evaluate polymer flow performance through porous media, displacement tests are conducted at laboratory bench scale at oil reservoir conditions (i.e., reservoir fluids at the corresponding reservoir temperature and pressure), to obtain valuable information about the efficacy of the polymer as a mobility control agent and its ensuing efficiency in displacing oil. Displacement tests allow quantifying two indicators of polymer flow performance, the resistance factor (F_r) and the residual resistance factor (F_{rr}) [4,6]. The resistance factor, F_r , indicates the mobility reduction imparted by polymer flow [4] and provides information on the effective viscosity or mobility control capability of the polymer solution in the porous media relative to water. The residual resistance factor, F_{rr} , gives information of the polymer-induced permeability reduction [4] due to polymer adsorption onto solid surfaces (i.e., physical adsorption) or mechanical retention (i.e., large size of the macromolecules relative to pore size). A moderate to low F_{rr} is

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desired for the polymer to be efficient in lowering the mobility of the injected water during polymer flooding. A large polymer retention would be detrimental because it could result in significant permeability reduction of the porous media, unfavorable polymer propagation retardation, and potential injectivity issues in oil reservoirs [7]. Therefore, the efficiency of oil recovery per gram of injected polymer is inversely related to polymer retention [4]. Polymer retention is also related to the molecular weight of the polymer, the clay content of the reservoir, and the cationic charge of the polymer's pendant groups.

The resistance factor, F_r , is defined in Eq. (1), where λ_w and λ_p are the mobility of the water and polymer solution, respectively [4].

$$F_r = \frac{\lambda_w}{\lambda_p} = \frac{k_w/\mu_w}{k_p/\mu_p} \quad (1)$$

where μ denotes the viscosity of either water or polymer solution, and k the permeability of the porous media (in millidarcy, mD) that can be determined from Eq. (2).

$$k = 1000 \frac{L}{A} \mu Q \frac{1}{\Delta P} \quad (2)$$

where Q is the volumetric flow rate (ml/s), ΔP is the pressure difference across the sand-pack at steady state conditions, μ is the fluid dynamic viscosity (centipoise, cP), L is the length of the sand-pack (cm), and A is the cross-sectional area of the sand-pack (cm²).

By inserting Eq. (2) in Eq. (1), at fixed flow rate, the resistance factor can be rewritten as Eq. (3):

$$F_r = \frac{\Delta P_{(\text{Polymer flooding})}}{\Delta P_{(\text{Brine before polymer flooding})}} \quad (3)$$

The residual resistance factor is defined by Eq. (4), as the ratio of the mobility of water (or brine), λ , before polymer injection, over the mobility of water (or brine) after polymer flooding:

$$F_{rr} = \frac{\lambda_b(\text{Before polymer injection})}{\lambda_b(\text{After polymer injection})} \quad (4)$$

F_{rr} can also be rewritten in terms of the pressure difference across the sand-pack before and after polymer solution injection (Eq. (5)):

$$F_{rr} = \frac{\Delta P_{(\text{Brine after polymer flooding})}}{\Delta P_{(\text{Brine before polymer flooding})}} \quad (5)$$

A comparison of the F_r and F_{rr} values among three types of polymers used in polymer flooding (xanthan gum, hydrolyzed polyacrylamide (HPAM), and hydrophobically modified acrylamide-based copolymer (HMSPAM)) was conducted by Wei et al. [8]. The F_r results clearly suggested that HMSPAM had higher effective viscosity compared to HPAM and xanthan gum. This might be due to the specific viscoelastic properties (and higher elasticity) of this polymer. On the other hand, HMSPAM showed significantly higher F_{rr} compared to the other polymer solutions, an indication of high permeability reduction, which would be an issue in oil field applications related to ineffective propagation. This indicates that effective polymers for EOR applications should optimize both these factors.

The overall oil displacement efficiency in EOR is defined as microscopic and macroscopic displacement efficiency of fluids contacting the oil in the micro- and macro-scale, respectively [5,9]. Microscopic displacement efficiency deals with mobilizing oil at the pore scale, while macroscopic displacement efficiency refers to mobilization of oil in the volumetric scale. In general, any macro- or micro-displacement that enhances oil sweep effectiveness increases oil recovery.

The viscoelastic properties of polymers are extremely important for efficient oil recovery and have been considered in the literature. It has been found that appropriate polymer viscoelastic properties in solution impose a large force on oil droplets in reservoirs and pull them out of the porous media [9–11]. In other words, polymers with the appropriate viscoelastic properties can pull other materials both behind and beside them due to high molecular weight and chain entanglements, while non-polymeric fluids are not capable of pulling out the oil from a pore [10]. It has been found that viscoelastic polymers with higher elasticity showed higher efficiency in oil displacement. In a research study, the behavior of water and three polymers with different viscoelastic properties was compared with respect to removing oil from a dead end pore [9]. The values of the storage (elastic) modulus over the loss (viscous) modulus ratio (G'/G''), i.e., inverse $\tan \delta$ values, for the three polymer solutions were equal to 0.92, 1.75, and 2.72. The results showed that the polymer with G'/G'' ratio equal to 2.72 performed better in pulling the oil out of the dead end pore, compared to the other polymers, due to its higher elasticity. On the other hand, water flooding made almost no change in the displacement of the residual oil in the dead end pore.

In a previous part of this research, a general framework for structure-property relationships was established and tailor-made AAm/AAC copolymers with optimal ranges of properties were synthesized [12–16]. Copolymers of AAm/AAC with high molecular weight (above 4×10^6 g/mol), a rather narrow and well controlled cumulative copolymer composition (AAm mole fraction range in the copolymer chains between 0.65 and 0.95), i.e., copolymers with a limited composition drift, and with a random distribution of AAC monomer units along the chain (a sequence length specification) were produced by reasonably fast polymerizations that reached high conversion (between 68% and 92%) [12].

The objective of this study was to evaluate in detail the performance of these designed AAm/AAC copolymers as mobility control agents for heavy oil recovery under realistic reservoir conditions. Sand-pack polymer flooding tests provide valuable information about polymer viscosity enhancement and polymer retention in porous media. Subsequently, heavy oil displacement tests provided additional information about the efficiency of these AAm/AAC copolymers in mobilizing and displacing heavy oil from unconsolidated porous media under simulated oil reservoir conditions.

2. Material and experimental methodology

2.1. Product design considerations

Based on previous knowledge of structure–property relationships, tailor-made AAm/AAC copolymers with desirable properties were synthesized to ensure the highest achievable efficiency of oil recovery under oil reservoir conditions [12–16]. Table 1 summarizes the properties of these designed copolymers, which have high AAm content (cumulative copolymer composition, cum $F_{AAm} = 0.67–0.93$), a random distribution of anionic charges along the copolymer chain, high average molecular weights (MW = 4.5×10^6 to 9×10^6 g/mol), various shear viscosities (1.3 to 3.9 Pas at a shear rate = 1 1/s), and various viscoelastic properties, loss over storage modulus ratio or $\tan \delta$ (0.5 to 0.9 at a shear rate = 1 1/s). The rheological properties of these polymers and the heavy crude oil used in the experimental runs were determined using a Bohlin Rheometer Gemini 150 Nano manufactured by Malvern (UK). The main characteristics that were considered for product design were high shear viscosity (maximum viscosity enhancement) and low polymer retention within the permeable media.

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