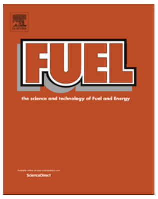
Fuel 207 (2017) 402–412

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Interfacial rheological insights of sulfate-enriched smart-water at low and high-salinity in carbonates

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ARTICLE INFO

Article history:
Received 19 June 2016
Received in revised form 13 June 2017
Accepted 20 June 2017

Keywords:
Asphaltenes
Visco-elasticity
Coalescence
Smart waterflooding

ABSTRACT

Lowering the injection water salinity or modifying its chemistry can improve waterflooding displacement efficiency. This water modification has been frequently alluded to increase rock water-wetness. However, the presence of sulfate anions in the aqueous phase is shown here to also alter the crude oil–water interfacial rheology drastically, in ways similar to that associated to the reduction of water salinity. Under the right conditions, oil recovery could, in principle, be increased to a considerably degree by alteration of fluid–fluid interactions at high salinity. The purpose of this research is to contrast oil recovery behavior in cases when smart-water is designed based on either increasing the sulfate anion concentration in a high-salinity brine or by decreasing salinity considerably, when using seawater as the base aqueous phase. Interfacial rheological and coreflooding results are compared to the case of seawater injection. The effect of various ions on the interfacial shear rheological response of several crude oils and modified seawater were examined. Carefully designed corefloods using Indiana Limestone were run to evaluate the effect of each brine on recovery behavior. Mild temperature and short ageing time were imposed to hinder wettability alteration. Interfacial rheological results show that the visco-elasticity of the crude oil-brine interface is higher for a low-salinity brine compared to the higher-salinity counterpart represented by seawater. However, when the sulfate anion concentration is increased, the interfacial visco-elasticity increases noticeably. Coreflooding results show that brines leading to more a visco-elastic interface, including low salinity and sulfated seawater, yield higher oil recovery factor. Ion analysis of the effluent brine shows that for the model rock used, brine composition does not change significantly from contact with rock surfaces. The recovery response is found to be consistent with changes in interfacial rheology. After the injection of high salinity smart-water in secondary mode, the low-salinity water injection in tertiary mode apparently triggers connection and mobilization of oil ganglia, as hypothesized from the recovery response. Tracking water droplet size distribution seems to support this hypothesis. Low-salinity brine injection is generally conducive to increasing oil production. On the other hand, our findings reveal that the injection of sulfate-enriched water can modify fluid–fluid interactions and consequently the final oil recovery. However, this smart-water appears to lose effectiveness entirely, if injected as residual oil saturation is reached, indicating an apparent threshold in the oil saturation to draw benefits of high-salinity sulfated-water.

1. Introduction

At present, fossil fuels satisfy 85% of the World's energy needs. The Annual Energy Outlook [1] reports that U.S. energy consumption grows at a moderate rate compared to projections, due in part to reduction in energy intensity through the use of improved technologies. Recently, the crude oil price reached the lowest values in the last 12 years, but experts indicate that this will not be long-lasting, though it is uncertain when the trend might reverse. The U.S. primary energy consumption projects a slight decrement in petroleum consumption, which in 2013 represented 36% of the total energy consumed, while the projection is 35% and 33% in 2025 and 2040, respectively. It is important to notice that petroleum and natural gas support more than 60% of the total energy consumption at present and this is projected to remain unchanged until 2040.

On the other hand, more than 60% of the world's remaining oil reserves exist in carbonate reservoirs, namely limestone, chalk and

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http://dx.doi.org/10.1016/j.fuel.2017.06.094
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dolomite, where the average recovery is low, probably below 35% on average [2]. A considerable volume of these carbonates are offshore, where waterflooding based on seawater injection is dominant among processes beyond primary production for maintaining pressure or as part of enhanced oil recovery (EOR) processes, due to resource availability.

Extensive studies have focused on the composition of the injected water after Tang and Morrow (1997) [3] and Zhang et al. [4] showed promising low-salinity waterflooding results on Berea sandstone cores. Numerous authors have shown that brine and oil composition are key for the observed ultimate recovery. Additional encouraging results have been obtained by varying the brine ionic profile and temperature as Morrow et al. (1998) [5] confirmed. Proposed mechanisms associated with this process vary significantly [6–18]. Wettability alteration [4,19,20], interfacial tension (IFT) reduction, in situ emulsification [17,21] and fines migration [8,20,22] have been brought to bear an impact on recovery mechanisms. However, Mahzari et al. [23] proposed the possibility that some of the cited mechanisms are observations due to low-salinity water injection rather than the dominant mechanisms. We argue that other contributing effects need to be considered.

Multivalent cations in the injection brine, i.e. Ca^{2+} and Mg^{2+}, are believed to act as a bridge between the rock surface and the crude oil, and at high enough concentration their positive charge can shield the repulsive force altering local wettability towards oil-wetness in sandstone [24–26]. Lowering salinity through reduction of cation concentration suppresses the shielding potential of the cations and the repulsive force becomes dominant. This has been used to explain wettability alteration towards water-wetness and thereby explain additional recovery [24,26].

Carbonates are assumed to be either mixed- or oil-wet under reservoir conditions. Anions such as sulfate in combination with excess calcium may induce anion exchange. Sulfate can adsorb onto the surface and previously adsorbed oil can be released to react with calcium [16,26,27]. This mechanism, however, appears to be effective mostly at high temperatures [28–33]. Therefore, low-salinity waterflooding in carbonates might not require low-ionic strength to be effective and instead it might benefit from choices of ions concentration. Evidence in the literature indicates that this might not be the complete story [28,31,34]. Despite differences in details, the fundamental hypothesis centers around wettability alteration mediated by the presence of sulfate (and in some cases divalent cations), which lead to the release of oil from shifting wettability toward a less oil-wet condition. Sulfate can have multiple effects on the complex oil-brine-rock system, beyond rock-fluid interactions.

An alternative/additional mechanism might be found in non-trivial fluid–fluid interactions [34]. Incremental oil recovery due to sulfate ions in chalk increases recovery without resorting to wettability alteration, as strongly water-wet cores were used in their experiments. Cores remained water-wet, because of insufficient ageing with crude oil. Results show that sulfate concentration, temperature and crude oil composition are critical. A decrease in crude oil viscosity was observed in the presence of sulfate at high temperature with clear emulsification arising with the increase in sulfate ion concentration [33]. Our recent papers [35–38] show that a connection between recovery and increase in interfacial elasticity is likely to exist. Additional works report higher interfacial visco-elasticity at low salt concentration, and using commercial microfluidic devices, the oil recovery resulted higher with low-salinity water flooding than that associated with high-salinity water [39]. Polar components in the crude oil can increase visco-elasticity and these are necessary for the overall recovery to improve [35,37,40]. Spiecker and Kilpatrick report the formation of elastic films of asphaltenes in water–oil interfaces [41]. Garcia-Olvera and Alvarado [37] show that partition of naturally occurring organic acids (often alluded as naphthenic acids) between the oileic and aqueous phases depends on the formation of the viscoelastic interface. The latter is tied to the fraction of asphaltenes and to lesser degree resins in the oil. In more quantitative terms, the polarity, shown through proxies such as refractive index, impacts the competition between organic acids and film-forming asphaltene and resins. These organic acids can have the effect of softening the interface, decreasing the elastic component of the interfacial rheological response and to a lesser degree the viscous component, shifting the ration toward a more viscous interface. In the case of acidic oils [42], it has been shown that the effect of sulfate on IFT, for an acidic oil, depends on the counter ion (cation). Changes in IFT are, however, small, but exhibiting a minimum as a function of salinity, though not in all cases. Mahzari et al. [23] and Sohrabi et al. [43] propose a crucial fluid–fluid interaction during low salinity injection, i.e. the formation of a micro-dispersion at the interface as an important mechanism for low salinity.

Addition of sulfate might turn out to be convenient for geochemical reasons, including the mitigation of anhydrite dissolution, which contributes to regulate water hardness [44]. However, a frequently encountered problem is the formation of hard scales when sulfate is supplied to reservoirs containing strontium or barium [45–48]. This all indicates that several considerations must be carefully pondered to decide how ion content should be modified to attain benefits from this adjusted brine chemistry. By the same token, since these decisions appear to depend on the rock-oil-brine system, a solution perceived as beneficial in one reservoir typology might not result in similar benefits for other reservoir types. This is certainly a consideration when comparing carbonate and sandy reservoirs.

Since interfacial elasticity hinders crude oil snap-off that generally leads to oil trapping during waterflooding, in this study, we investigate the effect of fluid–fluid interactions on oil recovery through modified seawater injection in secondary mode. Additionally, since snap-off and coalescence may occur in parallel during waterfooding, and both may impact the oil recovery [49,50], an emulsion stability analysis was conducted to obtain evidence of coalescence behavior in our coreflooding experiments.

Our research presents evidence of the sulfate effect on the crude oil-brine interface and how the latter relates to oil recovery. Most of the experiments were conducted at 25 °C, and the cores were not aged in the presence of oil to minimize wettability alteration and thereby highlight fluid–fluid interaction effects. Synthetic seawater and modified seawater, including diluted seawater as low salinity, were used to exemplify waterflooding offshore conditions. Four different crude oils were used to illustrate the similarity in recovery behavior. However, most of the results here correspond to those of a heavy crude oil from the Gulf of Mexico.

2. Materials

2.1. Crude Oil

Four reservoir dead crude oils were used in experiments. The first two, GB and WG, were obtained from two neighboring Wyoming sandy reservoirs, and two other viscous oils, ZD and K, were obtained from offshore carbonate reservoirs in the Gulf of Mexico. The oils were centrifuged at 7500 rpm for 5 h and passed through a paper filter (11 μm) to remove traces of water and particles. No precipitation of asphaltenes was observed during preparation or storage, so asphaltenes were assumed to be stable under experi-