Water-Soluble Silicate Gelants for Disproportionate Permeability Reduction: Importance of Formation Wetting and Treatment Conditions

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ABSTRACT

Two commercial water-soluble sodium-silicate-based gelant systems, Systems A and B, were tested for their potential as Disproportionate Permeability Reduction (DPR) agents on Berea outcrop cores. The DPR experiments were conducted using a steady-state, two-phase (oil/gelant) placement method to (a) ensure the presence of moveable oil and (b) quantitatively control the placement saturation conditions at which the silicate gel sets. The treatment performance was evaluated using pre- and post-treatment two-phase (brine/oil), steady- and unsteady-state permeability measurements.

Bulk and core experiments showed that shrinkage of System B was significant in short-term tests conducted at various temperatures. System A, on the other hand, formed long-lasting, stable, rigid gels at corresponding temperatures.

Tests conducted on water-wet long-core samples at relatively low formation watercut (WC) of 22% revealed no positive DPR effect. System A was also tested in oil-wet Berea cores which were treated chemically to alter their wettability. DPR treatments at the same WC as the pre-treatment conditions (22%) resulted in an effective DPR behavior. However, DPR treatments at 22% WC in cores with pre-treatment 78% WC were more effective resulting in a lower oil-phase residual resistance factor (RRF_o) compared to the one from cases for which DPR treatments were conducted at the same pre-treatment WC.

INTRODUCTION

DPR is one method that the oil industry has used to control unwanted water production without reducing oil reserves from the treated region. Application of the DPR technology can be wide in scope with polymers or polymeric gels used traditionally as the treatment fluids. The use of an oil-soluble silicate-based system TMOS (Tetramethyl-orthosilicate) as DPR fluid has been presented previously [1, 2]. Recently, Askarinezhad *et al.* [3] provided a detailed review of the various applications of water-soluble silicate-based gelants. These fluids are environmentally friendly and require no special permissions for their use in the field. This feature serves as one of the main advantages of water-soluble silicate systems over oil-soluble ones. Iler [4] provided details on the various steps required for gel formation from monomers to large particles, and finally to a gel.

The application of water-soluble, silicate-based rigid-gels is the main focus of this work. Askarinezhad *et al.* [3] tested the potential DPR effect of a commercially-available, water-soluble, silicate-based system (System A in this work) at different wettability conditions and presented a novel approach for DPR fluids placement, namely co-injection of oil and DPR fluid. In this work a new, water-soluble sodium silicate system (System B) is also tested its DPR effectiveness at similar treatment conditions. The most suitable silicate system, System A, was then tested as a DPR agent in oil-wet Berea cores to evaluate the effect of wettability on the DPR treatment. Experimental results showed a clear DPR effect following the formation treatment. System A was also placed at a lower watercut (22%) when the pre-treated core was producing at a 78% watercut. Treatment performance was evaluated by comparing ratios of pre- and post-treatment effective phase permeability measurements, defined as residual resistance factors (RRF). Note that DPR aims at reducing produced water without hindering, significantly, oil production; DPR treatments resulting in high RRF_w and low RRF_o values are considered as favorable.

ROCK/FLUIDS PROPERTIES – CHARACTERIZATION

Two commercially available, environmentally friendly, sodium silicate systems one with high (System A) and the other with low (System B) SiO_2:Na_2O molar ratio are used as the DPR fluids; Table 1 lists the two silicate systems' properties and activators used.

Table 1: Basic properties of the sodium silicate gelants (DPR fluids).

Silicate System	SiO_2:Na_2O Molar Ratio	pH	Gelant Viscosity (cp)	Activator	Gelant Type
A	High	10	1.7	Sodium Chloride	Newtonian
B	Low	11.5	2	Citric Acid	Newtonian

The rheology (gelation and kinetics of gelation process) of System A and formed gel properties have been investigated by Hatzignatiou *et al.* [5]. Bulk measurements showed that syneresis of gels formed using silicate System A was practically zero at different temperatures and activator concentrations, whereas System B has the tendency to shrink even by 50% of the original sample volume. In addition, bulk test observations presented by Hatzignatiou *et al*. [5] showed that the maximum compressional pressure (strength) of System A gels was significantly higher than the one of System B gels.

Strongly water-wet and (altered wettability) oil-wet Berea sandstone core samples (22-25 cm length and 3.77 cm diameter) were used in all experiments presented in this work. Filtered 0.1M sodium chloride brine and filtered isopar H (synthetic oil) with 1.29 cp viscosity at room temperature were the main "reservoir" fluids used.

Water-wet cores were treated chemically to alter their wettability to oil-wet. Measured phase-permeability curves together with recovery curves and spontaneous imbibition results were used to characterize the newly-established core wettability, which all demonstrated the water-wet and oil-wet (treated) nature of the tested core samples.

DPR TREATMENT PROCEDURE

All experiments were conducted using a steady-state, two-phase DPR placement in order to (a) better control the water/oil saturation at which the silicate gel sets (i.e., to quantitatively control the placement saturation conditions in the formation) and (b) ensure the presence of moveable oil at which the injected DPR gelant gels.

A typical DPR treatment experiment consists of three main stages. The core is first saturated with brine; pore volume (PV) and absolute brine permeability are then obtained, and irreducible water saturation, S_{wi}, is established by single-phase oil injection. After that, a steady-state, two-phase, brine/oil injection at room temperature is initiated, at the desired water fraction (watercut), to establish the pre-treatment condition (treatment initial saturation, S_{wti}). Following that, a steady-state, two-phase, DPR-fluid/oil injection is performed at selected treatment watercut; the new saturation condition, named DPR treatment final water saturation (S_{wtf}), is established. Gelation of injected gellant and aging for one week at 60°C is then conducted. In the third, and final, stage the water residual resistance factor (RRF_w) is obtained through steady-state brine/oil injection in a step-wise fashion at several watercuts and until the residual oil saturation is reached. The last part of stage three is single-phase, oil, injection to determine approximate values for the oil residual resistance factor (RRF_o). Additional details related to the newly established procedure can be found in Askarinezhad *et al.* [3].

Table 2: Summary of DPR experiments.

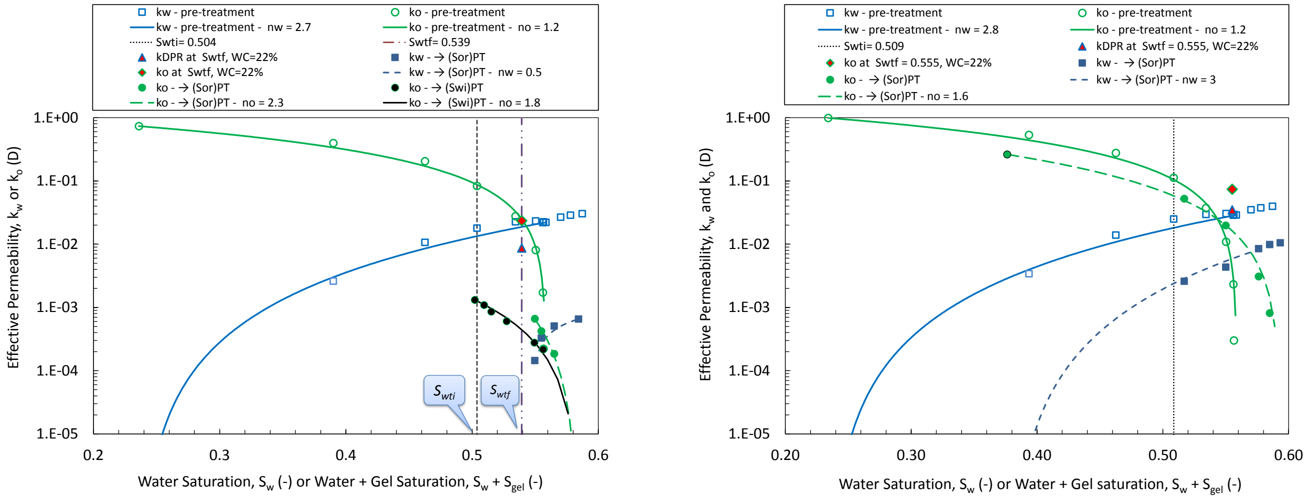
Exp. #	Silicate System	Wettability condition	Porosity (%)	Absolute brine permeability (D)	Residual oil saturation - Untreated core, S_{or} (%)	Pre-treatment and DPR treatment conditions					DPR Quantification	
						Pre-treatment production watercut, WC (%)	Treatment watercut, WC (%)	Saturation			RRF_w	RRF_o
								Brine-oil	DPR fluid-oil	Water saturation shift (%)		
								S_{wti} (-)	S_{wtf} (-)			
1	A	Water wet	22.2	0.642	41.3	22	22	0.503	0.539	3.6	100	460
2	B	Water wet	23.25	0.995	41.3	22	22	0.509	0.555	4.6	2.7	3.8
3	A	Oil wet	22	0.779	30.1	22	22	0.424	0.449	2.5	14	6
4	A	Oil wet	21.4	0.667	30.1	78	22	0.506	0.4	-10.6	10.6	3.4 - 4.5

EXPERIMENTAL RESULTS AND DISCUSSIONS

Table 2 provides a summary of the four DPR experiments discussed in this work together with relevant core properties. Experiments 1 and 2 were conducted in water-wet Berea cores and Experiments 3 and 4 in oil-wet cores. It is worth mentioning that in Experiment 2, the procedure was slightly different in the post-treatment floods compared to the other three experiments (single-phase oil injection was performed prior to the two-phase brine/oil injection). System B was used only in Experiment 2; in the remaining three, System A was used as the DPR fluid. In the following subsections, the details of each experiment together with the DPR treatment results will be presented.

Experiments 1, 2: Systems A and B, water-wet cores, pre- and DPR treatments 22%

The treatment conditions in Experiments 1 and 2 were the same; the DPR treatment initial water saturation (S_{wti}) was established at WC=22% using steady-state co-injection of brine and oil (Figure 1, dashed vertical lines). DPR treatment was performed at the same WC=22%. A water saturation shift due to DPR-fluid/oil co-injection can be observed with the treatment final saturation (S_{wtf}) displayed in Figure 1. Table 2 provides additional relevant data (see also [3]). A visual inspection of the pre- and post-treatment effective permeabilities suggests that Experiment 2 could yield favorable DPR conditions, especially if one considers field-expected post-treatment flow conditions at high WCs. The results obtained will be analyzed based on the post DPR treatment RRF values (Askarinezhad *et al.* [3]). Although the treatment watercut and saturation conditions in these two experiments were practically identical, the water saturation shift due to DPR-fluid/oil injection was more profound in Experiment 2. From the post-treatment floods, the reduction in both RRF_w and RRF_o were noticeably lower in Experiment 2 than in Experiment 1. The main reason is the significant shrinkage that occurs post-gelation with System B gels (Experiment 2). Bulk measurements at various temperatures on System B gels revealed a shrinkage of up to 50% of the total formed gel volume. The large saturation shift in post-treatment single-phase oil injection process in Experiment 2 serves as a confirmation of these observations; Bryant *et al.* [6] reported useful permeability reductions even at 95% syneresis of polymer gels. Effluent results in Experiment 2 revealed a relatively large gel erosion during the post-treatment floods.



(Experiment 1) **(Experiment 2)**

Figure 1: Water-wet, pre- and DPR- treatments at WC=22% (Exp. 1) System A [3]; (Exp. 2) System B.

Gel instability and syneresis may indicate that System B is a non-favorable gelant for DPR treatments considering also the weak contrast in the two-phase RRF values. On the other hand, results in Experiment 1 showed large RRF values, which coupled with the fact that System A yields very strong gels with practically no syneresis (Hatzignatiou *et al.* [5]), the syneresis could be linked to the degree of permeability reduction. Based solely on the RRF values, it can be argued that on one hand silicate gel systems with a high degree of syneresis may not be good DPR candidates, and on the other hand strong systems, causing large oil and water RRFs, did not result in possitive DPR effects.

Experiment 3: System A, oil-wet core, pre-treatment 22%, DPR treatment 22%

The water saturation shift during treatment was less compared to water-wet cores (Figure 2 and Table 2). Based on both RRF values, which are significantly higher in the water-wet cores compared to oil-wet ones, and the visually inspected separation of the pre- and post-treatment permeability curves, it is clear that wettability has a profound impact on the DPR effectiveness, resulting in significantly more favorable DPR effects in oil-wet formations. In this experiment, the reduction of both oil and water effective permeabilities is significantly lower than the ones in water-wet cores (Experiment 1), and it can potentially yield positive DPR. Extrapolated effective oil permeabilities to S_{wti} (red curve in Figure 2) show the improvement of RRF_o with reduced water saturation.

Experiment 4: System A – Oil-wet core, pre-treatment 78%, DPR treatment 22%

The evaluation of System A as a potential DPR fluid candidate was conducted following a slightly different procedure to reflect realistic field processes and examine possible hysteresis effects. The pre-treatment WC was increased to 78% with the treatment WC been kept at 22% (Table 2). Results shown in Figure 3 demonstrate slight improvements in RRF$_o$ compared to Experiment 3 and hysteresis effects to be practically negligible. Based on both visual inspection of the permeability curves and obtained RRF values, the achieved results demonstrated the potential for a more efficient positive DPR effect compared to the one obtained in Experiment 3. Results from this experiment serve as a starting point to the optimization of a two-phase DPR treatment in addition to serving more realistic reservoir/well conditions at which a treatment may be implemented by employing low WC treatments at realistically high pre-treatment production WCs.

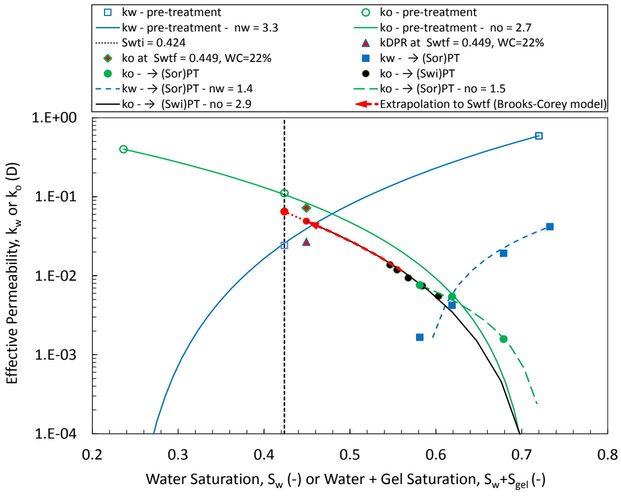


Figure 2: Experiment 3: Oil-wet, pre- and DPR treatment conditions at WC=22% [3].

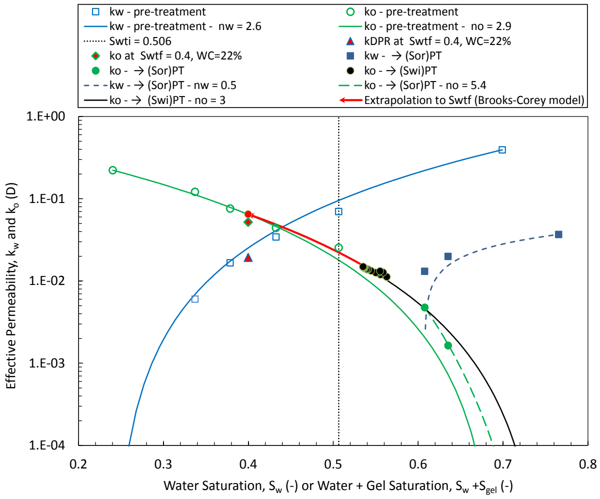


Figure 3: Experiment 4: Oil-wet, pre-treatment WC=78% and DPR treatment at WC=22%.

Discussion

DPR effectiveness was significantly different in water- and oil-wet cores mainly due to more favorable oil-phase continuity and distribution in oil-wet media compared to the corresponding one in water-wet formations. In water-wet cores, encapsulation of oil by gel may cause oil-phase discontinuities and porous medium conductivity reduction. Wettability tests have shown that silicate gel is strongly water-wet. Therefore, in oil-wet DPR treatments, formed gel in porous media yields a mixed-wet formation and a lower trapped oil saturation compared to water-wet formations. Another reason can be the lower mobile-oil saturation at S_{wtf} in the water-wet cases; the observed shift towards higher water saturations during treatment causes an even higher reduction in moveable oil saturation and a higher reduction in effective oil permeability.

In the water-wet experiment with System A, there is a rather visible hysteresis in post-treatment effective oil permeability. However, based on the qualitative analysis of our data, even if one is able to exclude the oil-permeability hysteresis effect (Experiment 1), the resulting RRF$_o$ values are still too high to lead to an efficient positive DPR effect. Therefore, it can be argued that hysteresis effects on water and, especially, oil effective permeabilities may not be the major reason for the observed DPR treatment results as also observed by Liang *et al.* [7]. Data from oil-wet cores showed that oil effective permeability hysteresis is much less pronounced than in water-wet ones.

CONCLUSIONS

In water-wet cores, DPR treatments resulted in high RRF values for both oil and water phases using gelant System A with absence of gel syneresis; gelant System B yielded almost identical, and low, RRF values with the formed gels displaying significant syneresis. In oil-wet cores, DPR treatments with System A resulted in significant lower oil and water RRFs than the ones observed in water-wet cores. The potential to optimize a DPR treatment effectiveness in a given oil-wet formation was demonstrated by deploying the DPR-fluid/oil mixture at low WCs when the formation produces at relatively high WCs. Generally, field executions require a careful design that balances the potential DPR treatment effectiveness with the treatment WC conditions, since low treatment WCs are also accompanied by small amounts of gel in treated porous media.

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