PORE-SCALE OBSERVATION OF RESIDUAL OIL IN LOW SALINITY SURFACTANT FLOODING

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This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in St. John's Newfoundland and Labrador, Canada, 16-21 August, 2015

ABSTRACT

Low salinity water injection provides favorable conditions for chemical enhanced oil recovery (EOR). Lower surfactant adsorption and lower chemical consumption is an advantage of combined low salinity water and surfactant injection. However at lower ionic strength the value of interfacial tension (IFT) is usually higher than the IFT at higher or optimal salinities. Recently it has been found that existence of small amount of calcium in low salinity surfactant can reduce the oil/water IFT. In this work, a coreflooding experiment is performed at the micro-CT scale. In tertiary injection the surfactant solution contained only NaCl, while the after-tertiary surfactant injection contained both NaCl and $CaCl_2$. After every step, the sample was scanned to observe the saturation and distribution of residual oil. It was observed that calcium-enhanced low salinity surfactant mobilized and recovered mainly the residual oil clusters which were affected but not recovered by tertiary surfactant. The oil which was not affected by tertiary surfactant mainly remained unaffected. It was also observed that oil recovery by low salinity surfactant in pore scale was higher than in normal core scale flooding experiment. In other words, microscopic sweep efficiency by low salinity surfactant was stronger than the macroscopic sweep efficiency.

INTRODUCTION

Both surfactant flooding and low salinity waterflooding may improve oil recovery. The goal of this work was to search for possible improvements in the performance of the combined low salinity water and surfactant by only modifying the ionic composition instead of adding extra chemicals. Observation of residual oil in pore scale by micro-CT was used to examine outcomes of the flooding experiment.

EXPERIMENTAL MATERIAL

Rock. The rock sample had a diameter of 4mm and a length of about 10mm. The sample was extracted from a Berea outcrop sandstone plug with permeability in the range of 200-300mD. Porosity of the scanned portion was 15.9%.

Oil. The oil phase is mixture of a crude oil (Table 1) and *1-Iododecane*. The volume fraction of *1-Iododecane* and crude oil is 6/4 in the mixture. *1-Iododecane* increases the x-ray attenuation coefficient of oleic phase.

Table 1. Composition in weight % and physical properties of the crude oil, [1]

Composition (%)		Physical properties	
Saturates	61.19	TAN [mg KOH/g]	1.08
Aromatics	32.42	TBN [mg KOH/g]	1.16±0.35
Resins	4.93	Density, 15°C [g/cm3]	0.8582
Asphaltenes	1.46	Density, 60°C [g/cm3]	0.8252
		API gravity [°API]	33.5
		Viscosity, 15°C [mPas]	19.90
		Viscosity, 60°C [mPas]	4.07

Brines and Surfactant. Details of the experimental brines are given in Table 2. 500 mg/l of *sodium dodecylbenzenesulfonate* (*SDBS*) is used in surfactant injection steps.

Table 2. Ionic composition of the brines and IFTs; IFT of doped crude was impossible to be measured by spinning drop as denser phase (oil) is not transparent and water/surfactant drop is invisible.

Brine	NaCl mg/l	$CaCl_2.2H_2O$ mg/l	SDBS mg/l	TDS mg/l	Ionic strength mmol/l	IFT, only crude mN/m	IFT, only 1-Iododecane mN/m
in-situ	32500	-	-	32500	556.1		84
LSW-Na	3250	-	-	3250	55.61		88.7
LSS-Na	3250	-	500	3250	57.05	1.6	15.6
LSS-Ca	3087.5	136.2	500	3690	57.05	0.33	-
HSW-Na	32500	-	-	32500	556.1	-	84

EXPERIMENTAL PROCEDURE

The rock sample was mounted in the micro-CT core holder, vacuumed and then saturated with *in-situ* brine (Table 2). Oil was then injected to drain mobile water. EOR injection was started with low salinity sodium chloride brine (*LSW-Na* in Table 2). Low salinity surfactant injection with sodium chloride (*LSS-Na*) was then performed. The next step was also low salinity surfactant injection. The difference was that small amount of sodium was replaced by calcium (*LSS-Ca*). Final injection was high salinity sodium chloride brine (*HSW-Na*). The experiment was performed at 27°C and atmospheric pressure. At the end of *LSW-Na*, *LSS-Na*, *LSS-Ca* and *HSW-Na* the injection was stopped and core holder was isolated for about 1hour to scan the sample. The sample was also scanned before saturation (dry scan) and afterward at initial state with connate water and initial oil. The details of injection experiment are given in Table 3. The scans were performed by micro-CT Skyscan 1172 with a resolution of 5.44µm/pixel.

Table 3. Details of EOR injection, the PVI (pore volume injected) is calculated roughly based on the pore volume of the whole sample (≈0.02cm3) with length of 10mm, while the scanned length is 6mm.

Injection	Flow rate (ml/min)	Equivalent pore velocity (ft/day)	Duration (min)	PVI	Scan name	Initial So	Final So	Rec. % OOIP
Oil injection	0.004-0.04	10-95	88	36.6	1-soi	0	0.864	-
	0.002	4.7	60	6	-	-	-	-
LSW-Na	0.004	9.4	30	6	-	-	-	-
	0.008	18.8	30	12	2-sorlsw	0.864	0.636	26.4
LSS-Na	0.008	18.8	93	37.2	3-sorlssna	0.636	0.529	12.4
LSS-Ca	0.008	18.8	93	37.2	4-sorlssca	0.529	0.426	11.9
HSW-Na	0.008	18.8	30	37.2	5-sorhsw	0.426	0.317	12.7
Total						**0.864**	**0.317**	**63.3**

RESULTS AND DISCUSSION

Image processing was performed using *CTAn*. The difference of gray scale index (GSI) between oleic and aqueous phases is about 100 units in the interval of 0-255. This large difference makes the fluids segmentation less subjective.

Although measurement of produced oil in micro-CT flooding experiments are almost impossible, oil recovery during all four steps of injection was observed. It was also observed that the recovered oil by *HSW-Na* in the last injection was in form of emulsion as opposed to larger oil clusters produced during low salinity water and surfactant flooding steps. The emulsions were formed at improved phase behavior of surfactant at higher salinity. The salinity of *HSW-Na* is close to the optimal salinity of surfactant solution with un-doped crude at elevated temperature of 60°C. Interfacial tension between crude and surfactant was about 0.005mN/m in that condition.

The saturation profiles are given in Figure 1. The average saturations and recoveries based on original oil in place are also given in Table 3. The recovery of low salinity waterflood was 26.5% which seemed to be lower than waterflooding recovery in normal cores. The reason might be the high density of oil phase which is $1.1g/cm^3$ due to addition of *1-Iododecane*. High density difference may not cause strong segregation in micro scale but it may bring fingering of the injected water. Another reason would be the high IFT of dopant agent with brine which is about 80mN/m (Table 2). On the other hand the recovery of *LSS-Na* is 12.4% which is 9% higher than the recovery in normal core scale performed using the same rock type, though the oleic phase and experimental conditions were different. Specifications of normal core flooding experiment are summarized in Table 4. There is also 11.9% oil recovered in the *LSS-Ca* step. This high difference of recoveries by surfactant in pore scale and normal core implies that microscopic sweep efficiency of oil by surfactant is stronger than its macroscopic sweep efficiency.

Table 4. Specifications of the normal coreflooding experiment – both µCT sample and normal core were extracted from an identical Berea block

length	9.9cm	Crude	crude in Table 1
diameter	3.8cm	In-situ brine	*in-situ* in Table 2
k	309mD	1st flood (LSW-Na) recovery	51.5% OOIP
Ø	15.5%	2nd flood (LSS-Na) recovery	3% OOIP
Soi	76.7%	*Flooding at 60°C*	*Aging after drainage: 3 weeks at 80°C*

Further, the saturation profiles in Figure 1 show that although in many parts of the sample oil mobilization occurred; in the two intervals of 3200-3500µm and 5800-6100µm low salinity surfactant with sodium (*LSS-Na*) could not mobilize oil. However in the next step (*LSS-Ca*) oil mobilization occurred. This extra oil mobilization at 3200-3500µm was most probably produced. If it was trapped again, the oil saturation at some part of the sample ahead of this point would have increased resulting in higher residual oil saturation than the previous surfactant injection (*LSS-Na*).
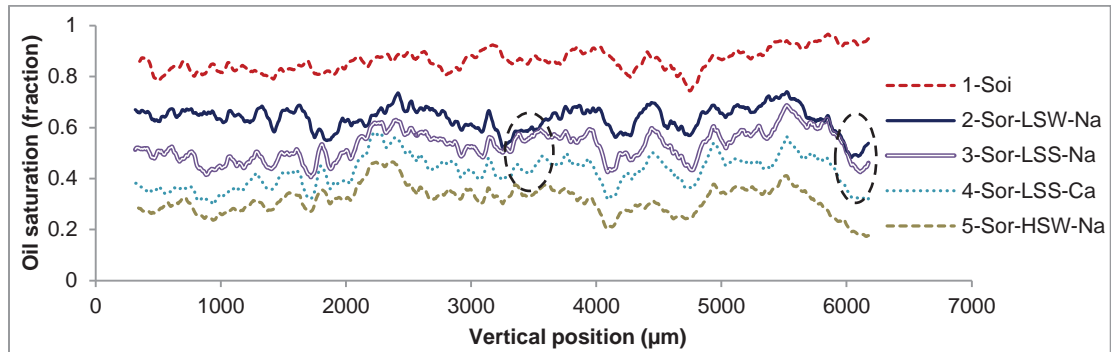
Figure 1. Oil saturation profile at initial condition (1-Soi) and after every injection (Sor's); the two dashed ovals represent two parts of the sample where LSS-Na was ineffective while LSS-Ca could mobilize and recover oil.
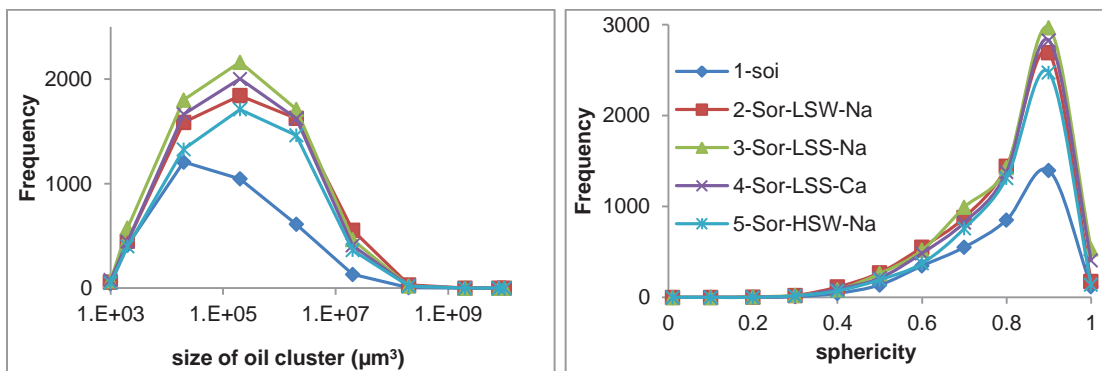

Figure 2. Oil cluster size (left) and sphericity (right) distribution at initial conditions and after every flooding

As shown in Figure 2 (left), number of oil clusters is minimum at initial conditions (*1-Soi*). The number has a sharp rise after low salinity waterflooding (*2-Sor-LSW-Na*). Afterwards, number of clusters increases slightly during low salinity surfactant with sodium (*3-Sor-LSS-Na*), while it decreases after the second surfactant injection with calcium (*4-Sor-LSS-Ca*). The sphericity of the oil clusters, Figure 2 (right), has similar trend in different steps of the experiment. Sphericity of a normal sphere is 1 and as the cluster becomes more irregular in shape, sphericity tends to 0. Normally sphericity of smaller clusters is more than that of larger ones.

1-Soi and 2-Sor-LSW-Na. Comparison of the low salinity water images with initial conditions shows that whenever oil is mobilized in a small pore the whole oil is often swept out the pore (Figure 3-A) while in medium pores some oil is left behind in form of trapped oil in the corner of pore (Figure 3-B). In larger pores the residual oil has more rounded profile and is mainly in the middle of the pore (Figure 3-C). This means that although the viscous force was high enough to invade the large pore it just peeled and displaced layers of oil instead of pushing the whole drop out of the pore. It was also observed that there was residual oil at some points where it was initially occupied by connate water (Figure 3-D). This type of residual oil was certainly mobilized initially but re-trapped later.
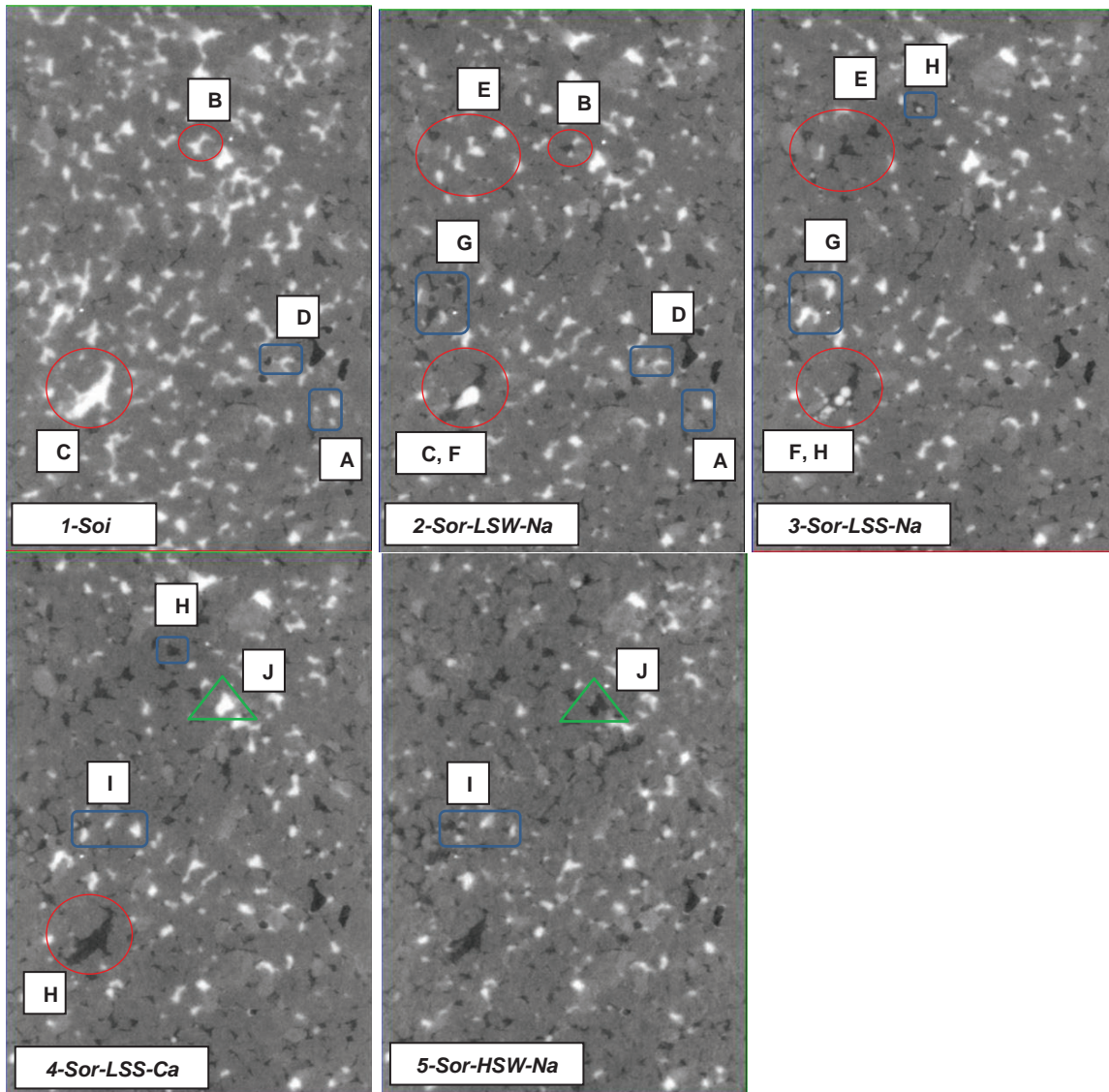
Figure 3. A vertical cross section of the cylindrical rock sample (D≈4000µm & L≈6000µm) after different steps; the injection was from top to bottom. <u>Oil is the white phase and water is dark one.</u>

2-Sor-LSW-Na and 3-Sor-LSS-Na. There are many small and medium pores where the whole residual oil after waterflooding or major part of it was displaced by first surfactant flooding, *Sor-LSS-Na* (Figure 3-E), while in larger pores oil was disintegrated into smaller (increase in number of oil clusters, Figure 2) and more rounded clusters (increase in sphericity, Figure 2) after layers of oil was peeled off (Figure 3-F). At some points, the mobilized oil was re-trapped again (Figure 3-G). The amount of this oil was 12.9% OOIP.

3-Sor-LSS-Na and 4-Sor-LSS-Ca. It seems that major part of the swept oil by calcium-assisted surfactant flooding (*LSS-Ca*) is the more spherical residual oil drops which changed their shape during previous surfactant injection (*LSS-Na*) (Figure 3-H). Reduction in sphericity and number of residual oil clusters after *LSS-Ca* was also

represented in Figure 2. Oil was rarely swept out of the pores which were not considerably affected by the first surfactant injection (*LSS-Na*). Moreover less oil was re-trapped after mobilization (only 4.8% OOIP compared to 12.9% in previous step). This is another advantage of *LSS-Ca* to *LSS-Na*. Although *LSS-Ca* could not effectively invade the relatively unaffected oil by *LSS-Na*, its oil recovery was 11.9% of OOIP which was a considerable amount of difficult residual oil after one step of surfactant injection (*LSS-Na*). This extra oil recovery was gained by only a minor change in ionic composition.

4-Sor-LSS-Ca and 5-Sor-HSW-Na. The mobilized oil by *HSW-Na* at some points is similar to the last surfactant injection where the more spherical oil clusters which were affected previously but not produced, were mobilized (Figure 3-I). However, oil mobilization was also observed in some pores where the two surfactant injections were ineffective (Figure 3-J). Coalescence of small and more rounded clusters occurred also (Figure 2). *HSW-Na* mixes with the surfactant from previous injection making a lower IFT surfactant solution. It seemed the mixing happened quickly as oil production was observed in form of emulsion just after some minutes of *HSW-Na* injection.

CONCLUSION

In the studied rock-fluid system with the mentioned experimental conditions it was observed that: calcium-enhanced low salinity surfactant recovered mainly part of the residual oil which was affected but not recovered by tertiary surfactant with only sodium. Oil re-trapping after mobilization by *LSS-Ca* is less than by *LSS-Na*. Comparison of recoveries in micro scale with those of normal core flooding implied that microscopic sweep efficiency of low salinity surfactant was higher than its macroscopic sweep efficiency. Therefore investigating the effect of mobility control during or after low salinity surfactant seems to be necessary as it may help producing the bypassed oil.

ACKNOWLEDGEMENT

REFERENCES
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