NEW EXPERIMENTAL EVIDENCE ON THE DOMINANT MECHANISM OF OIL RECOVERY BY LOW SALINITY WATER INJECTION IN CARBONATE ROCKS

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ABSTRACT

In the past two decades, several investigations have shown an improvement in oil recovery by low salinity water injection (LSWI) in core flood experiments and some pilot tests have been performed. Despite numerous publications on this matter, the underlying mechanisms leading to improved oil recovery have not yet been confirmed. It has been recently reported that certain crude oil-brine interactions take place during LSWI that lead to formation of water in oil micro-dispersions. The role of this mechanism, which is linked to the natural surface active components of the oil, has already been demonstrated in improving oil recovery in clastic rocks. In this work, we will test whether micro-dispersion formation could also be applicable to carbonate reservoirs.

This experimental investigation was performed on crude oil and rock samples obtained from a carbonate oil reservoir in the Middle East. Firstly, using an in-house methodology, a crude oil sample with high propensity to form micro-dispersion was identified. This crude oil (Crude-A) was then used in a series of oil/brine interaction tests involving formation brine and various diluted versions of it, to quantify the micro-dispersion formation capacity of the oil. Another sample from the same crude oil was then prepared by removing the compounds responsible for micro-dispersion formation (Crude-At). The two crude oil samples, one capable and the other incapable of forming micro-dispersion, were then characterised and prepared for core-scale experiments.

We observed that the crude oil with high micro-dispersion resulted in additional oil recovery during tertiary LSWI compared to the crude oil with low micro-dispersion. Therefore, the presence or absence of the oil compounds behind micro-dispersion formation can make the system respond positively or negatively to LSWI. The effluents of the coreflood experiments were also analysed. Interestingly, identical behaviour in terms of both pH and ionic concentrations was obtained with the two different oil recovery profiles, indicating that the micro-dispersion formation propensity of the crude oil is the main factor determining the efficacy of LSWI in carbonate rocks. The results provide useful new insights into the role of crude-oil/brine interactions during LSWI in carbonate reservoirs and their impacts on the response of a reservoir to LSWI.

INTRODUCTION

Enhanced oil recovery methods (EOR) are widely used in oil reservoir management. Recently, the process of injecting high salinity brine (HS) in secondary mode and low salinity brine (LS) in tertiary mode, has shown promising results in terms of recovering crude oil in carbonate reservoir rock [1]. The underlying mechanisms behind LSWI EOR at the pore level for certain conditions of crude oil and rock properties have been investigated for a period spanning around 30 years [2]. Among the mechanisms behind LSWI EOR, wettability alteration have been found to be more widely accepted as the underlying cause, from many experimental analyses and design data.

The fundamental principle of wettability alteration is the change in rock properties from oil-wet and/or mixed wet toward water-wet conditions, due to molecular interactions among the oil, brine, and rock minerals [2]. Further, the possible mechanisms behind wettability alterations can be broadly classified as rock-fluid interaction mechanisms and fluid-fluid interaction mechanisms. In a rock-fluid interaction mechanism, the involvement of multicomponent ionic exchange (anionic exchange and/or substitution reaction [3,4], mineral dissolution [5], and surface charge change [6]) in the rock matrix during LSWI EOR has been considered as the main cause of wettability alterations and hence, improved oil recovery during tertiary flooding. A close look at the proposed mechanism(s) in carbonate rocks would indicate many contradictory views.

In fluid-fluid interaction mechanisms, the formation of water micro-dispersions [7], due to the fluid-fluid interaction effect of oil-water contact flows, has been linked to improved oil recovery during LSWI EOR. It has been reported recently, Emadi and Sohrabi [12] that, certain crude oil-brine interactions take place during LSWI that lead to the formation of water-in-oil micro-dispersions. The role of this mechanism, which is linked to the natural surface active components of the oil, Mahzari and Sohrabi [13], has been demonstrated by improving oil recovery in clastic rocks. The aim of this work is to investigate whether the micro-dispersion mechanism can also control EOR by LSWI in carbonate reservoir rocks. To investigate this mechanism, a systematic analysis was carried out.

In this paper, we demonstrate the importance of the formation of micro-dispersion to additional oil recovery during LSWI EOR in carbonate reservoir rock. This is done by a targeted experimental design to study both fluid-fluid and rock-fluid interactions, to answer the question of whether a link can be observed between the role of micro-dispersion formation during oil-brine interaction and process of oil recovery during tertiary LS EOR in carbonate reservoir rock.

The paper is organised as follows: section 2, provides a brief introduction to the mechanism of micro dispersion due to oil-brine interaction, causing wettability alterations. Sections 3 explains the experimental design and the procedure used to investigate the cause of LSWI EOR. The results of these experiments are discussed in section 4 and, finally, we conclude this paper with a summary and future outlook in section 5.

BACKGROUND OF MICRO-DISPERSION AS A CAUSE OF WETTABILITY ALTERATION

Micro-dispersions are essentially packets (micelles) of water surrounded by certain indigenous surface active compounds of the crude oil [9]. In [10], the authors proposed two mechanisms that link the formation of these micelles to oil recovery by LSWI EOR.

- Wettability alteration due to migration of natural surface active components of the oil from the interface into the bulk of the oil
- Transport of micro-dispersion in the oil, in a manner similar to the osmotic effect, and their coalescence at the interfaces between crude oil and high salinity water, expelling oil from dead-end pores

Further the authors of [10], illustrated how the salinity variation would cause the pre-adsorbed natural surface active materials to migrate from the rock surface toward to the bulk of the oil phase, bringing about mobilization of trapped oil.

Error! Reference source not found.1 shows the formation of micro-dispersions during LSWI, at different scales. Figure 1A is a snapshot of a micro model experiment of LSWI at the macro scale. Figure 1B shows the interface between the oil and the low salinity brine during the low salinity brine flooding (images obtained from micromodel), showing that when low salinity brine contacts certain crude oils the colour of the oil becomes dark. Further, in Figure 1B, we can observe the formation of dark particles in the oil phase near the interface. Based on a series of micromodels and experiments, it was found that there is a correlation between the appearance and disappearance of these dark particles (which are referred to as micro-dispersion) and salinity of the brine [9]. Figure 1C, which is an ESEM (Environmental Scanning Electron Microscope) image of a sample taken from where the dark particles formed, shows white spots (determined as droplets of water using EDS). Further, each droplet of water (i.e. a nucleus of water) is composed of some ions taken from the LS brine and surrounded by particular components from the crude oil [8]. Analysis of these white spots showed that these micro-dispersions consist of both organic and inorganic compounds, arranged so that they have a centre, which is a water nucleus, and around it a layer of organic polar components coming from the oil (i.e. the oil encapsulates the water molecule) [10]. Figure 1D shows the micro-dispersion structure: a water molecule surrounded by polar molecular components of crude oil [8]. Figure 1E shows the arrangement of indigenous surface-active materials of oil in HS and LS systems. In high salinity systems, surface-active agents tend to adhere to the rock surface, creating an oil-wet condition. In the LS system, water, in the form of oil micro-dispersion, and indigenous oil surfactants leave the rock surface, accumulating around the water micro-dispersion [10].

Injection of LS brine results in the activation/release of the crude oil's natural surface active agents from the oil-water interface and brings about development of water micro-dispersion. This alters the oil surface charges, which itself changes the balance between repulsive and binding forces between the oil and the rock surface [11].

EXPERIMENTAL DESIGN

This section describes the experimental procedure followed in the lab to validate micro-dispersion as the mechanism for wettability alteration resulting in additional oil recovery during tertiary LSWI. This experimental study has two parts, namely, a fluid-fluid interaction test and a rock-fluid interaction test. These two parts are detailed in the two sections below.

(A) – Experimental Setup:
This section explains part 1 of the experimental set up and analysis **Error! Reference source not found.**. In this part, crude oils with the capability of forming micro-dispersions with low salinity brine were identified by conducting series of crude oil-brine interaction tests. A set of five crude oil samples was selected for the fluid-fluid characterization test (i.e. the crude oil-brine interaction test). These crude oil samples were filtered through centrifuging at $70\,^{0}$ Celsius to remove any solid or suspended particles from it. We then selected four formation brine samples of different salinities, ranging from 200,000 ppm to 1,000 ppm. We placed each brine sample in an in-house set-up and each crude oil sample was added on top of the brine, thus providing 20 combinations of brine-oil contacts. After 24 hours, the brine was drained slowly from the bottom, with a very low flow rate. Following the complete drainage of brine from the oil-brine samples, we took a sample of each crude oil which was interfacing with the brine prior to drainage. These samples of crude oil were finally used to measure the amount of micro-dispersion formed during the oil-brine interface interactions. Karl-Fischer Titration was employed to quantify the amount of micro-dispersion. After the complete analysis of the oils in part 1, Crude oil A was identified as the one with the highest propensity to form high micro-dispersions, compared to other samples of crude oil, when contacted with low salinity brine. A detailed explanation of this experimental methodology can be found in the paper [8]
Further to this, to conduct a fluid-rock interaction test, we prepared an additional crude oil, At, from Crude oil A, in such a way that crude oil At had a low capability to form micro-dispersion when contacted with low salinity brine compared to crude oil A. The preparation of crude oil At was carried out by selecting only the upper two thirds of Crude oil A, where no micro-dispersion was formed during the contact of Crude oil A with the low salinity brine sample.

(B) Recovery validation by core flooding:
This section explains part 2 of the experimental procedure and analysis. In part 2, the crude oil with high micro-dispersion was shown to recover additional oil during tertiary LSWI. In this validation process, two crude oils, Crude oil A and Crude oil At were selected to undergo LSWI for EOR.

First, two long cores with similar properties were selected for tertiary LSWI (12 inches long by 1.5 inch in diameter from a Middle East carbonate reservoir). The selected cores were then cleaned by flush cleaning at high temperature with toluene and methanol. The basic properties of each core were then measured, Table 1, which demonstrates acceptable similarities between the cores in terms of porosity, brine permeability, and initial water saturation. Next, the initial water saturation was established using mineral oil, followed by

aging the two cores by injecting the Crude oils A and At through the respective cores at the reservoir temperature for 21 days. During the aging period, the differential pressure (dP) across each core was measured and the crude oils were injected continuously at a rate of 1.5 PV per week until the dP across the cores became stable. An average initial oil saturation of 0.91 was established in the two core samples. Each core was then subjected to forced displacement by water using a flow rate of 4 cc/hr at a temperature of 80 ^{0}C and pressure 1000 psi. The sequence of fluid injection consisted of secondary high salinity water injection, followed by tertiary low salinity water injection for an extended time period. Throughout the experiment, the oil recovery and dP profiles were recorded. In addition, the pH value and ionic composition of the core effluent were measured. The HSWI was continued until no further oil production was observed. After no oil production was seen in the core effluent, three bumped floods were then performed at rates of 50, 70, and 80 cc/hr to check for any capillary end effect. LSWI was injected in tertiary mode with the same injection rate. In tertiary modes, the improved oil recovery by low salinity was found to be directly related to the presence of micro-dispersion.

RESULTS AND DISCUSSION

Figure 1 summarises the variation in micro-dispersion formed during the contact of Crude oil A and Crude oil At with the brines of different salinity, ranging from 1,000ppm to 208,600 ppm. From Figure 3, we can clearly identify that crude oil A has a great deal of potential to form micro-dispersion at low salinity conditions compared to Crude oil At. Furthermore, the amount of micro-dispersion formed by Crude oil A increases as the salinity of the brine decreases. However, in contrast, Crude oil At did not show any formation of micro-dispersion at all salinity levels of the formation brine. The reason for selecting very dilute salinity (1,000ppm) is to demonstrate the role of the crude oil's ability to form micro-dispersion in helping to enhance the oil recovery during tertiary LSWI. Since Figure 3 shows that crude oil A has more capability to form micro-dispersion, one may expect high oil recovery during tertiary LSWI compared with this oil compared to crude oil At, which has a poor capability to form micro-dispersion.

Figure 2 (a) shows the plot of oil recovery and the plot of dP versus injected pore volume during secondary high salinity flooding in the two cores, displacing Crude oil A in the first core and displacing Crude oil At in the second core. From the figure, we can observe that the trend of the oil recovery profile does not show significant variation, irrespective of the large difference between crude oil A and crude oil At in their propensity for micro-dispersion. However, the slight difference in the oil recovery could be due to the initial wettability of each core and the pore geometry (i.e. structure). Prior to tertiary recovery, we ensured that all the other artefacts, associated with low injection resulting end effects, which might contribute to oil recovery in the tertiary LSWI, for example, capillary end effects, which may contribute to low salinity EOR [12], are reduced substantially. This reduction of the artefacts is carried out by employing a series of bump floods. The results of the bump flood in the two cores after secondary recovery, shown in Figure 2 (b), indicate that there is no capillary end effect

Figure 3 shows the outcome of the tertiary LSWI in this carbonate system. 6.3% additional oil recovery was achieved in the coreflood experiments where Crude oil A was used. On the other hand, when crude At was used, tertiary low salinity water could not improve the oil recovery. The results confirm the positive response of this carbonate system to LSWI when a crude oil with high propensity to form micro-dispersion was used. Thus as far as these carefully designed experiments could reveal, micro-dispersion formation would be the main cause for additional oil recovery.

The core effluent was analysed to obtain the profiles of ionic concentration and pH value, as presented in Figure 4 and Figure 5. To obtain a better understanding of the geochemical process in terms of rock-brine interactions, we first measured the pH of the water, because this provided an indication regarding the rock-brine interactions. The pH value during tertiary LSWI showed a higher value, due to calcite dissolution which had occurred inside the core. In terms of ionic concentration of the effluent, the ionic concentration for LSWI is a diluted version of that in HSWI (1,000 ppm): thus, the ratios of the ions in both floods are the same. Because of this, we have plotted the ratio of the ions, instead of plotting the concentration of the ions in the conventional way (i.e. C/Co). The ratios of both calcium and magnesium to sodium have increased compared to the ratio in the injected concentration. This shows that there is a possibility of mineral dissolution from the rock causing this increase. Moreover, the ratio of sulphate to chloride exhibits an increase after one pore volume of LSW was injected, which reached the maximum value at two pore volumes, and then gradually decreased and fell to its lowest value. This increase in sulphate would be related to the release of ions from the rock surface and was probably due to dissolution of anhydrite.

Thus, we observed a similar increase in pH value, together with mineral dissolution, and also anhydrite dissolution, when using Crude oil A and Crude oil At in the respective core flood tests during LSWI. However, the resultant increases in oil recovery for the core flood test using only Crude oil A, which has high micro-dispersion, imply that the fluid-rock interaction mechanism has not played a significant role in additional oil recovery during tertiary LSWI. The results of this study reveal that pH increase, mineral dissolution (include calcite and anhydrite) are not needed for LSWI to work in carbonate rock. Nasralla [13], also conclude that mineral dissolution is not the dominant mechanisms in increasing oil recovery in LSWI. However, this conclusion was based in brine unable to dissolve calcite, whereas some brines which dissolved calcite produce no additional oil recovery. Furthermore, the finding of this study that anhydrite dissolution is not necessary for improved oil recovery conflict with Austad's [14] conclusion that increase oil recovery is linked to anhydrite dissolution, Moreover, the result shown in Figure 3 indicates that Crude A, with high propensity to form micro-dispersion, results in high oil recovery and leads us to conclude that the micro-dispersion mechanism would be the primary mechanism for wettability alteration, thereby increasing the oil recovery during tertiary LSWI.

CONCLUSION

In this paper, the underlying mechanisms leading to improved oil recovery during tertiary LSWI were analysed. The results provide new experimental evidence on the underlying mechanism causing the improved oil recovery during LSWI, which is micro-dispersion formation. Two crude oil samples having high and low propensity to form micro-dispersion were selected and the core flood experiments have verified the link between the formation of micro-dispersion and the improvement in oil recovery. Furthermore, the experiments also confirmed that geochemical interactions such as mineral dissolution, sulphate interactions, and pH variations are not the primary mechanism for such additional recovery. From the experimental outcome, it is conceivable that identifying the crude oil propensity to form micro-dispersions can be a feasible method to evaluate the effectiveness of LSWI.

ACKNOWLEDGEMENTS

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Table 1 properties of the cores and brines used in this study

Brine used				
Salt	Formation water, g/l	Diluted formation water, g/l		
$CaCl_2*2H_2O$	101.28	5.96 times dilution	41.72 times dilution	208.6 times dilution
$MgCl_2*6H_2O$	13.96			

NaCl	150.2			
Na_2SO_4	0.55			
	208,600 ppm	35,000 ppm	5,000 ppm	1,000 ppm
Cores properties				
	Core flood test -1		Core flood test-2	
Length, cm	30		30	
Diameter, cm	3.75		3.75	
Porosity, frac.	0.268		0.272	
K brine,mD	2.6		2.43	
Swi, frac.	0.09		0.1	
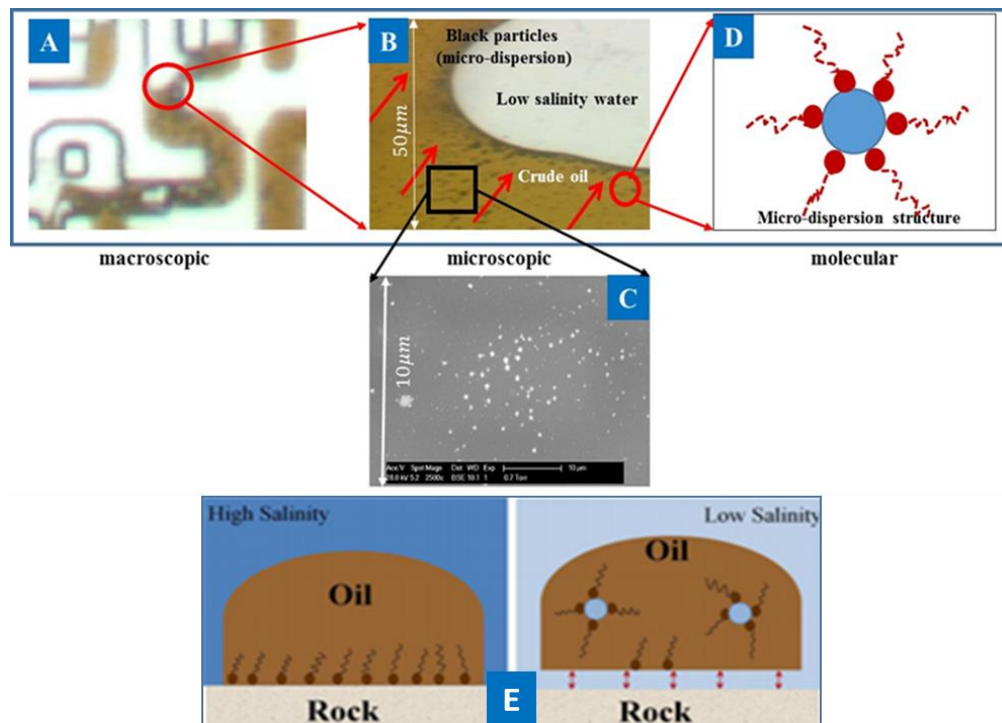
Figure 1 Spontaneous formation of micro-dispersion during the displacement of crude oil by low salinity water. A: formation of micro-dispersion in the oil phase during LSWI in the micromodel. B: a highly magnified section of the micromodel showing the instantaneous formation of micro-dispersion when LS brine contacts the crude oil. C: crude oil contact with LS brine under ESEM image, note the light spots (i.e. dark particles as seen in micromodel). D: illustration of micro-dispersion structure, representing the dark (B)/light (D) particles; these include organic and inorganic components: the polar compounds of the crude oil encapsulate the water molecules. E showing the arrangements of indigenous surface active materials of oil in HSWI and LSWI.
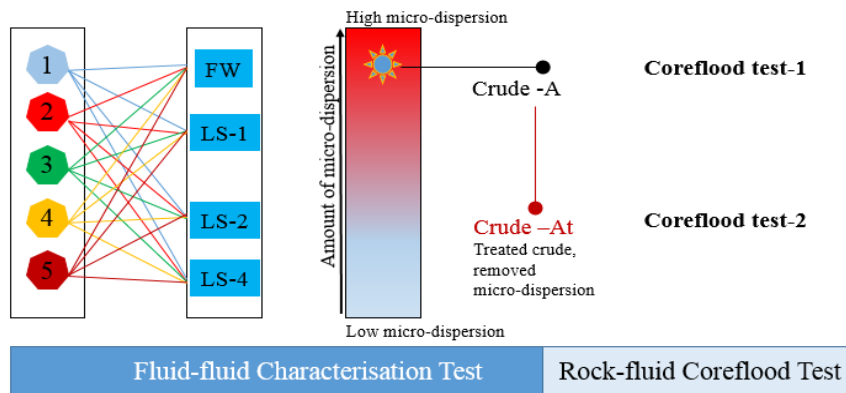
Figure 2: Experimental design: screening propensity of crude oils for micro-dispersion at different salinities and design of the fluid displacement efficiency test, accordingly. Crude A is prone to form high micro-dispersion; Crude At is the same as Crude A; the only difference is that we have removed micro-dispersion from the original crude oil. Crude A and Crude At are sharing the same reservoir oil but crude At is treated by removing micro-dispersion (i.e. polar components); columns 1 and 2 respectively represent oil and water samples. The left side (columns 1 and 2) shows a mixed matrix where heptagons 1 to 5 represent different crudes brought together with 4 different water compositions.
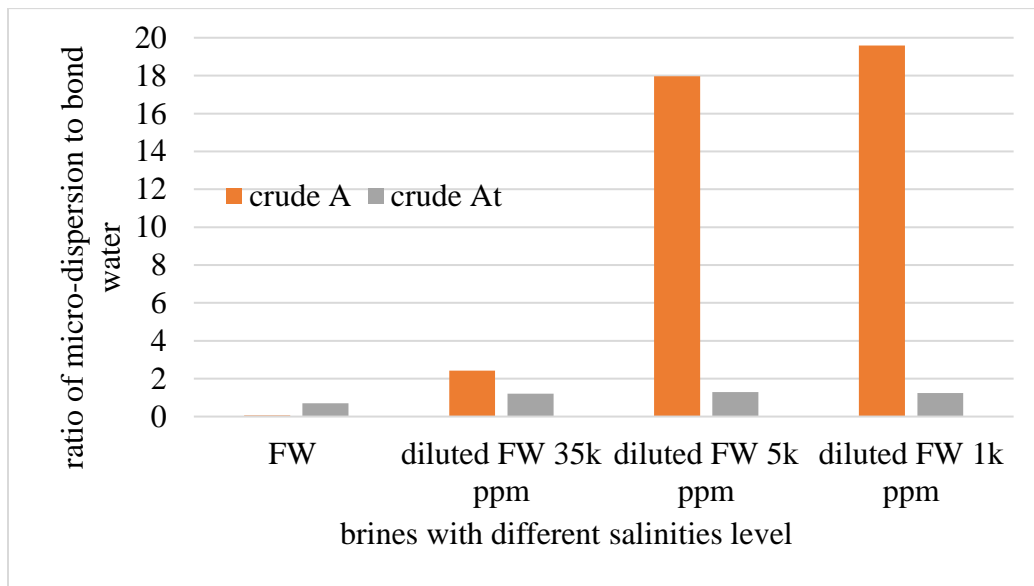
Figure 1: The two selected crude oils were contacted with brines of different salinities to quantify the amount of micro-dispersion in each crude oil. Y-axis shows the ratio of amount of micro-dispersion to the bond water (original crude oil pre-contacted). A LSW with 1,000 ppm was selected for the tertiary coreflood tests.
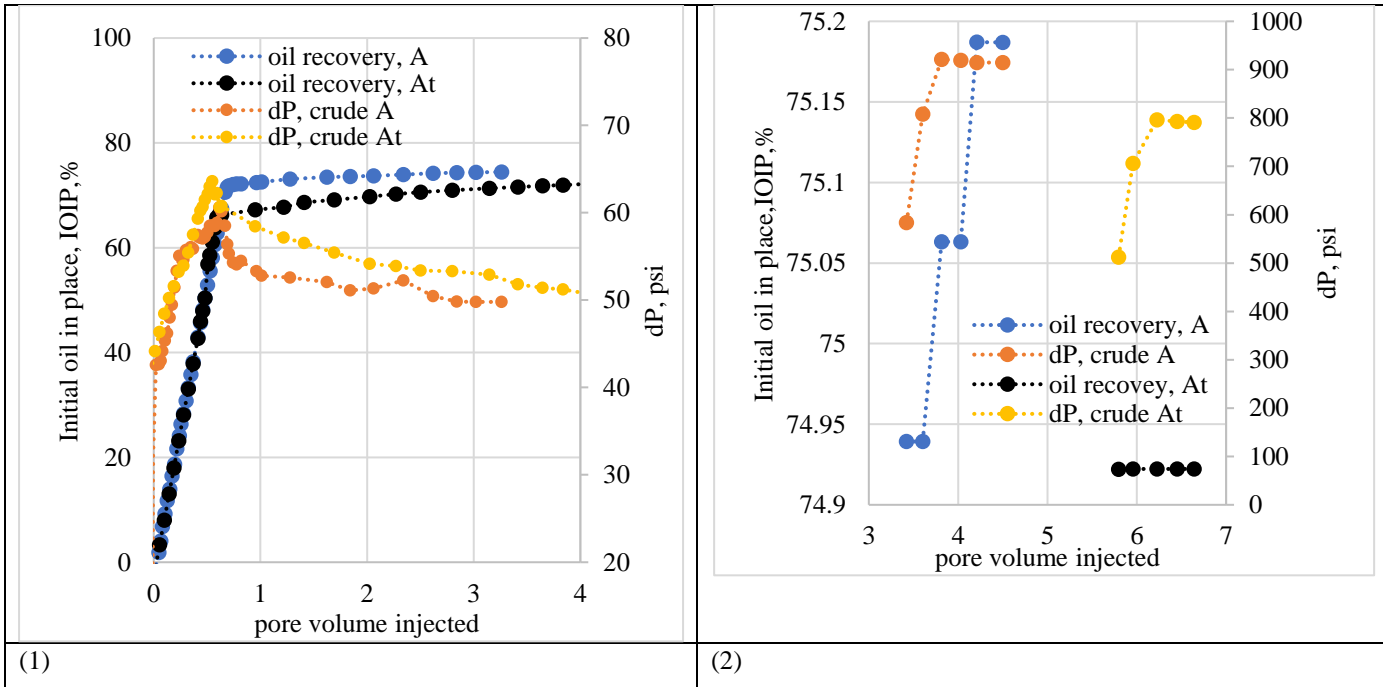
(1)　(2)

Figure 2 plot 1 shows secondary high salinity water injection result for both crude A and At respectively and plot 2 result of secondary high salinity bump flood at the end of 4cc/hr (equivalent to reservoir flow advance rate 1ft/day)
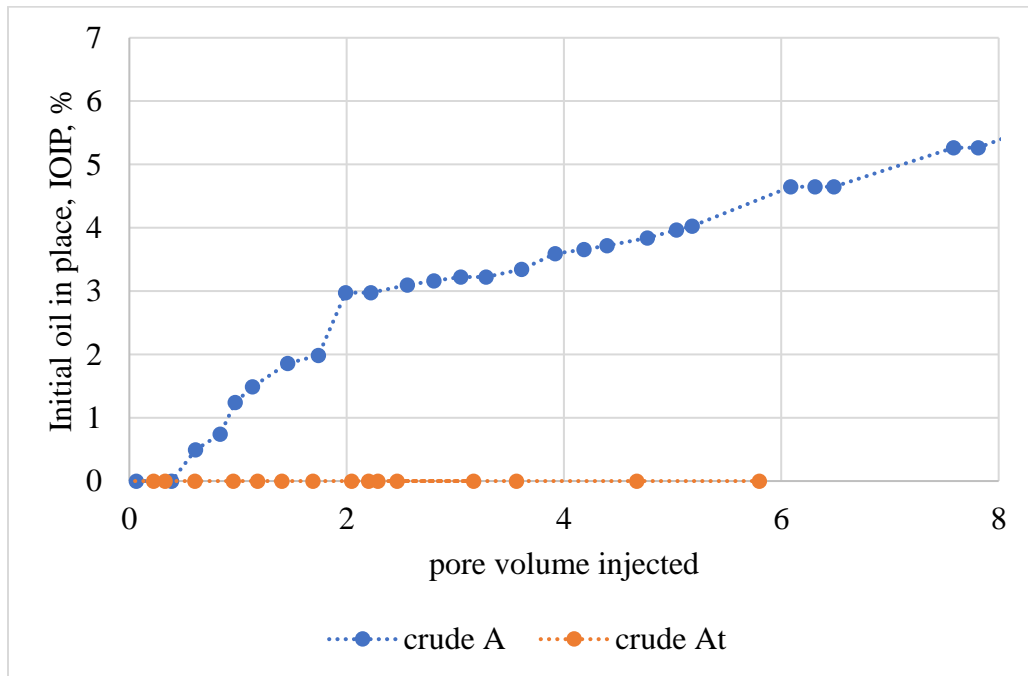

Figure 3 Tertiary low salinity water injection: effect of the presence and/or absence of micro-dispersion on the improved oil recovery during LSWI
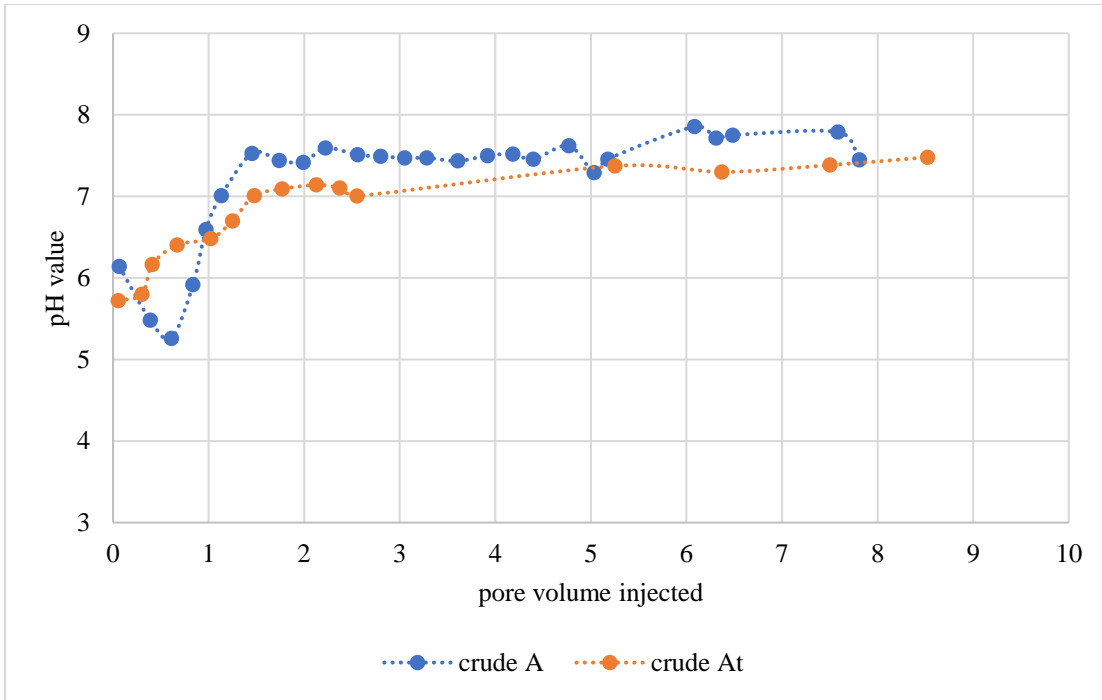
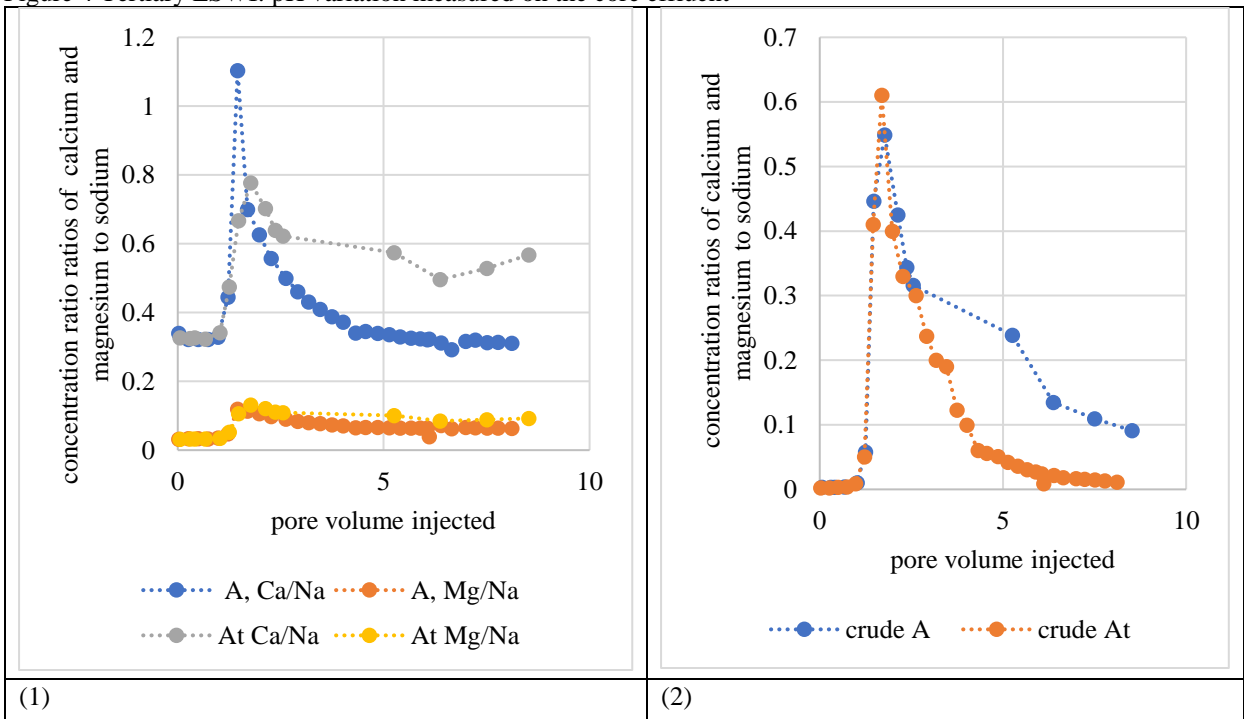Figure 4 Tertiary LSWI: pH variation measured on the core effluent

(1)

(2)

Figure 5: Graph 1 shows tertiary LSW Ca^{2-}/Na^{1+} and Mg^{2+}/Na^{1+} versus pore volume LS injected. Graph 2 tertiary LSWI SO_4^{2-}/Cl^{1-}