

USE OF ENZYMES TO IMPROVE WATERFLOOD PERFORMANCE

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ABSTRACT

A variety of enhanced oil recovery (EOR) methods have been developed and applied to improve waterflood efficiency. These methods aim at improving both microscopic displacement efficiency and macroscopic reservoir sweep. In addition to reducing residual oil saturation and increasing contact with unswept oil, fluid flow improvement has also been a focus of EOR technologies. A change in wettability may lead to a favorable change in fluid flow properties. Another significant focus has been to improve spontaneous imbibition to enhance oil recovery from matrix rock in fractured reservoirs.

We have been investigating to what extent enzymes-proteins can change the wettability state of an oil reservoir formation and possibly lead to increased oil recovery by waterflooding. Enzymes consist of water soluble proteins which may act as catalysts and encourage interactions between oil and water that may release oil from the grain faces of a porous medium.

This work reports the results of contact angle measurements to quantify the changes in wettability resulting from different concentrations of enzyme-in-brine solutions. Several different enzyme-protein mixtures have been investigated. The experimental results confirm a considerable decrease in contact angle with enzyme solutions compared to an untreated brine. In all cases, the change due to added enzymes was towards a more water-wet state. The paper will also discuss core flood results using enzyme-in-brine solutions for waterflooding Berea sandstone cores aged in crude oil.

INTRODUCTION

Wettability has been the object of much research. Several papers have discussed the influence of wettability on oil recovery. The major factor which controls the location, flow, and distribution of fluids in a reservoir is wettability [1]. Wettability is a significant issue in multiphase flow problems ranging from oil migration from source rocks to such enhanced recovery processes as chemical flooding or alternate injection of CO₂ and water [2]. Several researchers attempt to alter the wettability favorably in the oil reservoirs to improve spontaneous imbibition of water and also the waterflood in order to enhance oil recovery. Austad et al. [3] and Xu et al. [4] reported different production profiles using surface active agents to enhance spontaneous imbibition into chalk cores and ascribed this difference in behavior to the change of wettability by surface active agents. Several authors [5-7] have reported effects of brine composition on wettability change and Alagic and Skauge [8] demonstrated the use of low salinity water plus surfactant to change wettability and improve oil recovery.

Enzymes-proteins can be introduced to improve waterflood performance especially in oil-wet reservoirs by changing the wettability to a more water-wet state and possibly lead to increased oil recovery [9]. Enzymes are a specific group of globular proteins that are synthesized by living cells to work as catalysts for the many thousands of biochemical reactions such as break down or synthesis of certain compounds. Like all catalysts, enzymes work by lowering the activation energy of a reaction, thus dramatically accelerating the reaction rate [10-11]. Chemical catalysts display only limited selectivity; whereas enzymes show specificity for the substrates and also products, which ensure that the final product is not contaminated with by-products. Enzymes with broad specificity have more flexible active site requirements and can therefore accept a wider range of substrate molecules [10-11].

Use of different types of enzymes in industrial application started many years ago. Use of enzyme processes in the oil and gas industry context has, however, only been suggested recently. Enzyme applications were reported in the oil industry in different categories such as removing damage by disrupting filter-cake formation in drilling; enzyme base acid production; sand consolidation; desulphurization of hydrocarbons containing high levels of sulphur; and water shut-off [12]. Feng et al. [9] also reported the use of enzymes to improved oil recovery at laboratory and field scales.

This paper presents the results of a study to provide improved insight into the impact of enzyme-protein type reactions in porous media. The specific objectives were to: (1) evaluate the results of the static experiments such as contact angle and interfacial tension measurements, (2) determine key parameters that may govern the process, and (3) perform core flood experiments to investigate wetting change and possible oil mobilization. The paper is divided into two parts; the first presents a review of static experiments and results thereafter, the paper presents and discusses the core flooding experiments.

EXPERIMENTAL

Materials

Solid

Four core plugs, B1, B2, B3 and B4 were cut from the same block of Berea sandstone. Physical properties of the cores are reported in Table 1.

Glass microscope slides (28×48) from Menzel-Gläser, Germany were used in the experiments to measure the contact angle.

Oil

Two types of stock tank oil, A and B (Table 2) from two oil reservoirs in the North Sea were used in the static experiments. Both oils were filtered through a 0.5 µm filter to remove any coarse particles prior to use. Based on acid and base numbers, cores were aged in crude Oil B and then waterflooded [13-14].

Brine

Synthetic sea water (SSW) was used in all static and dynamic experiments. Table 3 shows the composition of the used brine.

Enzyme-Protein

Three types of enzymes, Zonase1, Zonase2 and Greenzyme were used in the static experiments. Zonase 1 and 2 were provided by a company located in Bergen, Norway. Detailed specifications of Zonase 1 and 2 were not available because of company restrictions. Another type of enzyme, Greenzyme was also used in the experiments. Greenzyme is a water-soluble formulation made from DNA-modified proteins extracted from hydrophobic microbes in a batch fermentation process [15]. Among mentioned enzymes, Greenzyme was selected for use in dynamic experiments.

Procedures

Contact Angle

The KSV camera 200 was used to measure the water-oil contact angle based on sessile drop technique. A Hamilton micrometer (1 ml) inverted syringe was used to deposit the droplets on the glass slides. All experiments were performed at ambient conditions. To see the effect of the enzymes on the contact angle, some experiments were done with three different types of enzymes. The results were compared to reference contact angles performed with untreated brine, i.e. brine without added enzymes. In the experiments, different weight percentages (0-2%) of the enzymes were used as the heavier (aqueous) phase and crude oil A and B as the lighter phase. The oil droplets were deposited on the glass surface surrounded by the aqueous phase, and gave a dynamic water receding condition by displacing the water from the surface. In each experiment, after deposition of the oil droplet on the surface and waiting for a while (approximately 2 min) to stabilize the droplet, images of the water-oil contact angle were taken at 5 second intervals. For each concentration 7-10 parallel droplets have been examined, 10 images were taken of each droplet. It means that for each droplet there were about 70-100 measurements. So, each reported data point in Tables 4-9 is the average of all measured data that represents a static equilibrated contact angle (θ_{ER}) initiated by a water receding angle. The experimental error of the contact angle is estimated to $\pm 4^\circ$.

In the second group of experiments, glass plates aged in crude oil A and B for about 30 days at 80°C were used as the solid surface when crude oil A and B were used as the probe respectively. Using aged glass plates had some advantages such as more stable oil droplets on the solid surface and more visible effect of the enzymes on the contact angles. To use the aged glass plates for the contact angle measurements, bulk crude oil must first be rinsed off. This was done by gently rinsing with Toluene, soaking in fresh Decane (about 2 min) and finally rinsing with distilled water [16]. It should be noted that this procedure is not unique, as it depends to what extent adsorbed material is removed by rinsing with toluene. As a result, variation in the reference contact angle was observed (see Tables 5-7 and 9).

IFT

The KSV camera 200 pendant drop instrument was used to measure the interfacial tension between crude oil and brine. The crude oils were equilibrated with brine prior to measurements. Brine and crude oil with a 1:1 volume ratio were shaken for 3 days, and then stored horizontally for 2 days at room temperature to allow be stabilization.

Viscosity

The MCR300 delivered by Physica, Anton Paar, which is a shear rate controlled rheometer equipped with two different sets of geometry was employed to measure viscosity.

For viscosity lower than 10 mPa·s the concentric cylinder geometry, DG26.7/T200/SS, with 23.83 mm and 27.59 mm internal and external radius respectively was used. The temperature was controlled by a Peltier water circulating/heat-regulating apparatus ($\pm 0.1^\circ\text{C}$), mounted on 78210 TEZ 150 P cell.

For viscosities higher than 10 mPa·s which is rheological characterization of crude oil samples, CP75-1 cone plate-to-plate geometry with 74.987 mm diameter and 0.994° angle was used. This time, the Peltier element was coupled with CF80 TEK 150 P-C cell to stabilize temperature during measurements.

Dynamic Displacement Tests

Preparation

All the cores were put in the oven at 60°C for about 72 hours to ensure that they were totally dried. Vacuum pump was used to saturate the cores 100 % with brine. Porosity of the cores was determined from the weight difference of the saturated and dried cores. All the cores were installed into triaxial-type core holders with 20 bars confining pressure. To establish an initial water saturation, S_{wi} , high viscosity oil (Marcol 152) was used to displace the brine. After attaining a desirable S_{wi} , Marcol 152 were exchanged with the crude oil by injecting of at least five pore volumes of crude oil into the cores. Permeability of the cores was determined in both cases, before and after establishing of S_{wi} . The saturation procedure and all the displacements were done in ambient temperature (22°C).

In order to establish non water-wet condition in the cores, all the cores were enclosed in core holders and aged in an oven at 80°C for one month. During the aging period, crude oil inside the cores was exchanged with fresh crude oil once a week. After the aging step, the cores were flooded with an additional four pore volumes of freshly filtered crude oil.

Spontaneous Imbibition of Brine

Two cores were used to examine spontaneous imbibition of brine, whereby the wetting fluid (brine) spontaneously imbibe into the pore spaces and displaces the less-wetting fluid (crude oil) from the pore spaces of a porous medium.

Cores B3 and B4 at S_{wi} status were immersed in brine and enzyme-brine respectively to compare the oil production vs time behavior and to see the effect of the enzyme on spontaneous imbibition. The expelled oil was collected and its volume was measured. Results were recorded as the total amount of oil produced at various time intervals.

Core Flooding

The displacement tests were performed in four sandstone cores using brine, enzyme-brine and crude oil B. The core flooding apparatus consisted of a Quizix high pressure pump system equipped with a pair of cylinders to provide continuous flow of different fluids into the cores and a separator at the production line to collect and record

volumetric production profiles of different phases from the cores. Pressure changes during flooding were also monitored with a FUJI pressure transducer and were logged continuously during injection.

A nominal flow rate of 0.1 ml/min was used to inject brine into cores B1-B3, followed by higher injection rates of brine to ensure that there is no more incremental oil production. While core B1 and B2 started from S_{wi} , core B3 had been used to measure spontaneous imbibition of brine prior to the waterflooding sequence. After waterflooding to residual oil saturation, 1wt% GZ-brine solutions were injected into the cores to see the effect of enzyme on the oil production. Core B2 was further flooded with a 10wt% GZ-brine solution to see if increasing the enzyme concentration had an effect on oil recovery. Core B4, for which spontaneous imbibition of 1wt% GZ-brine had been measured, was injected with the enzyme-brine solution directly. All the flooding experiments were performed in ambient temperature (22°C).

RESULTS AND DISCUSSION

Contact Angle Measurements

Crude oil A

Table 4 shows the results for crude oil A with glass slides without any aging as the solid surface and brines with different Greenzyme concentration as the aqueous phase. As the results clearly show, the difference in contact angle with and without enzyme is in some cases about 30° which is quite significant. The dimensionless term $\Delta\theta/\theta_{REF}$ was defined, where $\Delta\theta$ is $\theta_{REF} - \theta_{ENZYME}$ and θ_{REF} is the contact angle measured with a brine phase without added enzyme. As the concentration of Greenzyme increases, the change in contact angle is more visible and $\Delta\theta/\theta_{REF}$ increases accordingly to reach a plateau of roughly 0.5 at 0.75 wt% Greenzyme (Figure 1).

In the second group of experiments, glass aged in crude oil A for about 30 days at 80° C was used as the solid surface. This showed a more visible effect of the enzymes on change of the contact angle. Different enzymes with different concentration were examined in this group of experiment. Table 5-7 show the results for different types of enzyme. Unlike the first group of experiments, the reference contact angle in the second group is different in all cases. The main reason is the washing procedure for the aged glass plates as described earlier.

To examine the effect of enzyme on glass slides with different wettability states, identical concentration of enzymes was used in some cases for different reference contact angles. Results for Greenzyme (Table 5) show a significant change in contact angle by adding enzyme. However for reference contact angles > 90 degrees the effect of enzyme on the contact angle seems to decrease. Results for Zonase1 (Table 6) were not promising except for high concentrations. Using Zonase2 (Table 7) resulted in changes in contact angle, but less pronounced than for Greenzyme at the same concentration and for comparable reference contact angles.

Crude oil B

Greenzyme was selected for use in experiments with crude oil B. Tables 8 and 9 show the results for glass and aged glass as solid surfaces respectively. According to the results, contact angle changes are almost the same independent of concentration, for the case using ordinary glass without aging. For the case of aged glasses, reference contact

angles vary. For the cases that have almost similar reference contact angle the changes in contact angle are almost identical and independent of Greenzyme concentration. As an example, for the concentration of 1 and 0.01 wt% of Greenzyme in aged glass experiments, $\Delta\theta/\theta_{REF}$ shows almost the same value irrespective of the Greenzyme concentration.

IFT Measurements

Interfacial tension between crude oil (A and B) and brine adding different concentration of Greenzyme was measured. Figure 2 shows the results of the measurements. The Figure shows IFT of 24 and 11 mN/m for the crude oil A and B respectively. According to the Figure, IFT decreases with decreasing Greenzyme concentration for both oils. For crude oil A, the trend levels off at 0.5 wt% concentration at 7mN/m IFT and for crude oil B at 5 mN/m at 1 wt% Greenzyme concentration.

Viscosity Measurements

Viscosity of crude oils, brine and different concentration of GZ-brine solution were measured. It was about 1.1 mPa·s for the brine. According to measurements adding Greenzyme into the brine solution had no effect on viscosity and was observed to be Newtonian even in the case of adding 10 wt%. Table 2 also shows viscosity of the crude oils.

Dynamic Experiments

According to the results of contact angle measurements, Greenzyme seemed to have larger influence on changing the contact angle than the other two enzymes. So, it was selected among available enzymes for displacement tests. Even though lower concentrations showed good results in contact angle measurements, 1wt% concentration was selected in tests of the effectiveness of Greenzyme.

Brine Flooding Followed by Enzyme-Brine Flooding, Core B1

After continuous injection of brine into core B1, a total oil recovery of 42 % OOIP was obtained after about 10 PV injections. Most of the oil was produced before water break through (WBT) at 0.37 PV (Figure 3). This was followed by flooding with brine containing 1wt% Greenzyme (GZ-brine). Very low rate of oil production was observed after starting the GZ-brine injection. 11 % OOIP incremental oil were produced after 34 PV injections.

Brine Flooding Followed by Different wt% of Enzyme-Brine Flooding, Core B2

Core B2 gave a recovery of 47% OOIP total oil recovery after more than 10 PV of continuous brine injection (Figure 3). Water breakthrough (WBT) happened after injection of 0.33 PV. Although most of the oil was produced before WBT, more oil was produced after WBT compared to core B1. This could be an indication of a more oil-wet condition for core B2 as compared to core B1. The flooding was continued with injection of 1%wt GZ-brine injection. The rate of oil production was low with only 3.5% OOIP additional recovery after more than 40 PV injection. To test the effect of high GZ concentration, this was followed by injection of 10wt% GZ-brine with different injection rates (0.1-0.5 cc/min) into the core. No additional oil was produced after more than 22 PV injection.

Spontaneous Imbibition and Flooding Scenario, Core B3 And B4

Figure 4 shows the results of spontaneous imbibition of brine and GZ-brine into cores B3 and B4 vs dimensionless time, t_D . This scaling group was introduced by Ma et al. [17] to obtain a dimensionless time, t_D , which compensates for differences in rock and fluid properties:

$$t_D = t \sqrt{\frac{k}{\phi}} \frac{\sigma}{\sqrt{\mu_w \mu_o}} \frac{1}{L_c^2} \quad (1)$$

Where t is imbibition time, k permeability, ϕ porosity, σ interfacial tension, μ_w and μ_o viscosity to water and oil, respectively, and L_c is the characteristic length (all quantities in consistent units).

In the early stages of oil production by spontaneous imbibition of brine and GZ-brine into the cores, the production rate in core B3 is larger than in core B4. Consequently, after the first minute, oil recovery in core B3 is about 24% OOIP compared to 14% OOIP in core B4. This delay in oil production could be related to Greenzyme reaction time. However, the Figure shows larger total oil production by spontaneous imbibition of GZ-brine in core B4 (43 % OOIP) compared to core B3 (41% OOIP). However the oil recovery difference is 2 % OOIP which is not significant.

Cores B3 and B4 were flooded using different slugs of brine and GZ-brine after spontaneous imbibition. Core B3 was continuously flooded by brine but, there was no further oil production after about 15 PV injection into the core. Injection of GZ-brine was then performed for core B3 using different injection rates. Incremental production of 5.2% OOIP (Figure 5) was attained after 26 PV injection. Core B4 was flooded continuously with GZ-brine using different rates of injection. 5 % OOIP (Figure 5) incremental oil was produced over about 35 PV injection. In both cases, as Figures 5 and 6 show, with the first nominal injection rate (0.1 cc/min) no further oil production was observed, but increase in the rate of injection (0.3-0.5 cc/min) resulted in additional production.

Wettability and Water End Point Permeability

Comparison of brine end point permeability can be used as an indication of wettability. More water-wet behavior shows lower water end point permeability at the same water saturation, S_w . Table 10 shows water endpoint permeabilities at water saturations representative of the different stages of the flooding, i.e. after waterflooding and after flooding with GZ-brine. Comparison of the endpoints before and after 1wt% GZ-brine flooding shows no significant wettability change for cores B1, B2, and B3.

Core B4 which was not exposed to the untreated brine in all stages shows lower end point permeability than other cores with respect to related S_w which is almost in the same range of others. Core B2 showed lower end point permeability (29 mD) after 10wt% GZ-brine flooding compared to after flooding with 1wt% GZ-brine (60 mD), even though no additional oil was produced. Decrease in the water endpoint permeability in the case of 10wt% GZ-brine flooding without any change in saturation unit of brine (no oil production) may indicate that the core was becoming more water-wet.

CONCLUSION

Contact angle measurements indicate more water-wet behavior with enzymes solution, especially for Greenzyme (GZ).

Interfacial tension between crude oil and brine solution containing enzymes shows somewhat lower values compared to untreated brine, but adding enzymes into the brine has no effect on brine viscosity.

Results of spontaneous imbibition of untreated brine and GZ-brine show delayed imbibition of GZ-brine in the early stages, but higher total oil production.

Additional oil recovery from 3.5% to 11% OOIP was obtained by injection of the enzyme solution into the cores.

Endpoint permeability of the cores indicate little change in wettability of the cores after flooding with GZ-brine, except for the core B4 that was never exposed to untreated brine and core B2 when 10% GZ concentration was used as the displacing fluid.

For the cores in this study, less change in wettability than expected was observed which could be due to the rather water-wet behavior being exhibited even after the aging period.

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NOMENCLATURE

| | |
|-------------------|---|
| PV | pore volume |
| OOIP | original oil in place |
| SSW | synthetic sea water |
| WBT | water breakthrough |
| S_{wi} | Irreducible water saturation |
| θ_{REF} | Contact angle measured with a brine phase without added enzyme |
| θ_{ENZYME} | Contact angle measured with a brine phase added different enzyme concentrations |
| $\Delta\theta$ | difference between θ_{REF} and θ_{ENZYME} |
| θ_{ER} | static equilibrated contact angle initiated by a water receding angle |
| IFT | interfacial tension |
| t | imbibition time |
| k | permeability |
| Φ | porosity |
| σ | interfacial tension |
| μ_w | viscosity of water |
| μ_o | viscosity of oil |
| L_c | characteristic length |

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Table 1. Physical properties of Berea core samples

| Core ID | Length (cm) | Diameter (cm) | Porosity (%) | PV(ml) | Swi | Soi | Abs. Kw(mD) | Ko, Swi(mD) |
|---------|-------------|---------------|--------------|--------|------|------|-------------|-------------|
| B1 | 5.83 | 3.7 | 22.27 | 14.14 | 0.18 | 0.82 | 621 | 645 |
| B2 | 5.91 | 3.7 | 21.81 | 14.04 | 0.18 | 0.82 | 632 | 662 |
| B3 | 5.7 | 3.7 | 21.6 | 13.41 | 0.18 | 0.82 | 576 | 617 |
| B4 | 5.9 | 3.7 | 21.7 | 13.9 | 0.2 | 0.8 | 619 | 555 |

Table 2. Properties of the crude oil

| Crude oil ID | Density at 20°C (g/ml) | Viscosity at 20°C (mPa·s) | Acid number (mg KOH/g oil) | Base number (mg KOH/g oil) |
|--------------|------------------------|---------------------------|----------------------------|----------------------------|
| A | 0.8436 | 51* | 0.123 | 1.096±0.05 |
| B | 0.8784 | 13.8 * | 2.84±0.01 | 0.95±0.10 |

*at shear rate 100 (s⁻¹)

Table3.Composition of brine

| Chemical compound | Na ⁺ | Ca ²⁺ | Mg ²⁺ | Cl ⁻ | HCO ₃ ⁻ | SO ₄ ²⁻ | K ⁺ |
|-----------------------------|-----------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|----------------|
| Concentration of ions (ppm) | 11156 | 471 | 1330 | 20128 | 139 | 2743 | 350 |

Table 4. Contact angle measurements for crude oil A-Brine+GZ-Glass

| Type of Enzyme | Enzyme concentration (wt%) | Reference contact angle without enzyme, θ (degree) | Average contact angle with enzyme (degree) | Difference, Δθ (degree) | Δθ/θ |
|----------------|----------------------------|--|--|-------------------------|------|
| Greenzyme | 0.01 | 62 | 46 | 16 | 0.26 |
| Greenzyme | 0.05 | 62 | 43 | 19 | 0.31 |
| Greenzyme | 0.1 | 62 | 42 | 20 | 0.32 |
| Greenzyme | 0.25 | 62 | 38 | 24 | 0.39 |
| Greenzyme | 0.5 | 62 | 36 | 26 | 0.42 |
| Greenzyme | 0.75 | 62 | 32 | 30 | 0.48 |
| Greenzyme | 1 | 62 | 32 | 30 | 0.48 |
| Greenzyme | 2 | 62 | 32 | 30 | 0.48 |

Table 5. Contact angle measurements for crude oil A-Brine+GZ-Aged Glass (aged at 80°C)

| Type of Enzyme | Enzyme concentration (wt%) | Reference contact angle without enzyme, θ (degree) | Average contact angle with enzyme (degree) | Difference, Δθ (degree) | Δθ/θ |
|----------------|----------------------------|--|--|-------------------------|------|
| Greenzyme | 0.05 | 68 | 45 | 23 | 0.34 |
| Greenzyme | 0.05 | 77 | 53 | 24 | 0.31 |
| Greenzyme | 0.1 | 65 | 34 | 31 | 0.48 |
| Greenzyme | 0.1 | 87 | 57 | 30 | 0.35 |
| Greenzyme | 0.5 | 84 | 45 | 39 | 0.46 |
| Greenzyme | 0.5 | 126 | 122 | 4 | 0.03 |
| Greenzyme | 0.5 | 93 | 48 | 45 | 0.48 |
| Greenzyme | 0.5 | 50 | 43 | 7 | 0.14 |
| Greenzyme | 0.5 | 68 | 40 | 28 | 0.41 |
| Greenzyme | 1 | 84 | 50 | 34 | 0.40 |

Table 6. Contact angle measurements for crude oil A-Brine+Zonase1-Aged Glass (aged at 80°C)

| Type of Enzyme | Enzyme concentration (Wt%) | Reference contact angle without enzyme, θ (degree) | Average contact angle with enzyme (degree) | Difference, $\Delta\theta$ (degree) | $\Delta\theta/\theta$ |
|----------------|----------------------------|---|--|-------------------------------------|-----------------------|
| Zonase1 | 0.1 | 128 | 120 | 8 | 0.06 |
| Zonase1 | 0.1 | 51 | 51 | 0 | 0.00 |
| Zonase1 | 0.5 | 121 | 137 | -16 | -0.13 |
| Zonase1 | 0.5 | 48 | 44 | 4 | 0.08 |
| Zonase1 | 1 | 123 | 138 | -15 | -0.12 |
| Zonase1 | 1 | 54 | 44 | 10 | 0.19 |
| Zonase1 | 2 | 129 | 107 | 22 | 0.17 |

Table 7. Contact angle measurements for crude oil A-Brine+Zonase2-Aged Glass (aged at 80°C)

| Type of Enzyme | Enzyme concentration (wt%) | Reference contact angle without enzyme, θ (degree) | Average contact angle with enzyme (degree) | Difference, $\Delta\theta$ (degree) | $\Delta\theta/\theta$ |
|----------------|----------------------------|---|--|-------------------------------------|-----------------------|
| Zonase2 | 0.1 | 86 | 86 | 0 | 0.00 |
| Zonase2 | 0.5 | 92 | 64 | 28 | 0.30 |
| Zonase2 | 1 | 54 | 42 | 12 | 0.22 |
| Zonase2 | 1 | 56 | 38 | 18 | 0.32 |
| Zonase2 | 1 | 82 | 58 | 24 | 0.29 |
| Zonase2 | 2 | 107 | 64 | 43 | 0.40 |

Table 8. Contact angle measurements for crude oil B-Brine+GZ-Glass

| Type of Enzyme | Enzyme concentration (wt%) | Reference contact angle without enzyme, θ (degree) | Average contact angle with enzyme (degree) | Difference, $\Delta\theta$ (degree) | $\Delta\theta/\theta$ |
|----------------|----------------------------|---|--|-------------------------------------|-----------------------|
| Greenzyme | 0.01 | 52 | 33 | 19 | 0.37 |
| Greenzyme | 0.05 | 52 | 33 | 19 | 0.37 |
| Greenzyme | 0.1 | 52 | 33 | 19 | 0.37 |
| Greenzyme | 0.25 | 52 | 34 | 18 | 0.35 |
| Greenzyme | 0.5 | 52 | 34 | 18 | 0.35 |
| Greenzyme | 1 | 52 | 34 | 18 | 0.35 |

Table 9. Contact angle measurements for crude oil B-Brine+GZ-Aged Glass (aged at 80°C)

| Type of Enzyme | Enzyme Concentration (wt%) | Reference contact angle without enzyme, θ (degree) | Average contact Angle with enzyme (degree) | Difference, $\Delta\theta$ (degree) | $\Delta\theta/\theta$ |
|----------------|----------------------------|---|--|-------------------------------------|-----------------------|
| Greenzyme | 0.01 | 79 | 37 | 42 | 0.53 |
| Greenzyme | 0.05 | 72 | 37 | 35 | 0.49 |
| Greenzyme | 0.1 | 61 | 41 | 20 | 0.33 |
| Greenzyme | 0.5 | 65 | 41 | 24 | 0.37 |
| Greenzyme | 0.5 | 67 | 45 | 22 | 0.33 |
| Greenzyme | 1 | 81 | 39 | 42 | 0.52 |

Table 10. End point permeabilities and Sw for different stages of the cores

| Core ID | Sw (%) after brine flooding | Kw at Sor, (mD), after brine flooding | Sw (%) after 1%GZ-brine flooding | Kw at Sor, (mD), after 1%GZ-brine flooding | Sw (%) after 10%GZ-brine flooding | Kw at Sor, (mD), after 10%GZ flooding |
|---------|-----------------------------|---------------------------------------|----------------------------------|--|-----------------------------------|---------------------------------------|
| B1 | 52.26 | 43 | 61 | 67 | --- | --- |
| B2 | 56.20 | 51 | 59 | 60 | 59.05 | 29 |
| B3 | 49.29 | 42 | 54 | 52 | --- | --- |
| B4 | --- | --- | 57 | 38 | --- | --- |

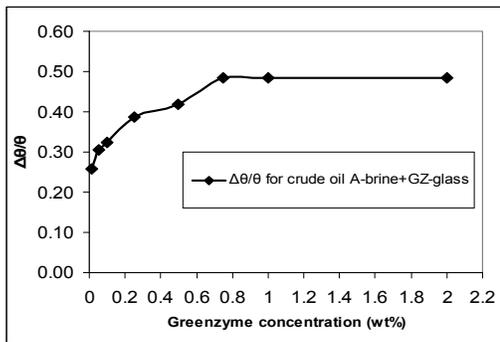


Figure 1. $\Delta\theta/\theta$ vs. Greenzyme concentration

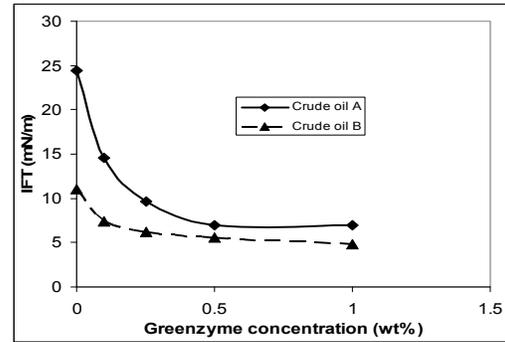


Figure 2. IFT for different concentration of GZ-brine and crude oil A and B

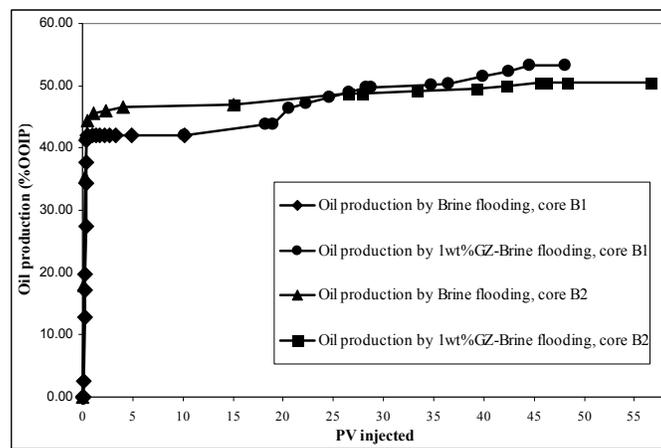


Figure 3. Production profile for different flooding scenarios Cores B1 and B2 (aged at 80°C)

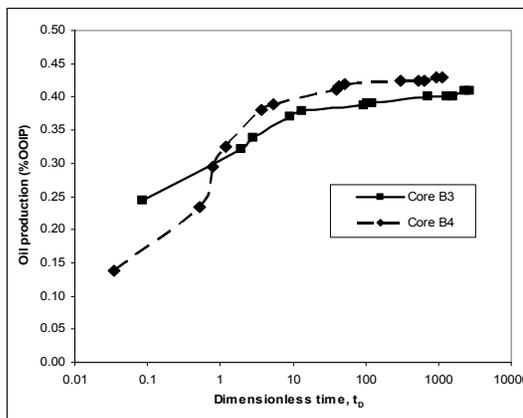


Figure 4. Oil production by imbibition vs dimensionless time Cores B3 and B4

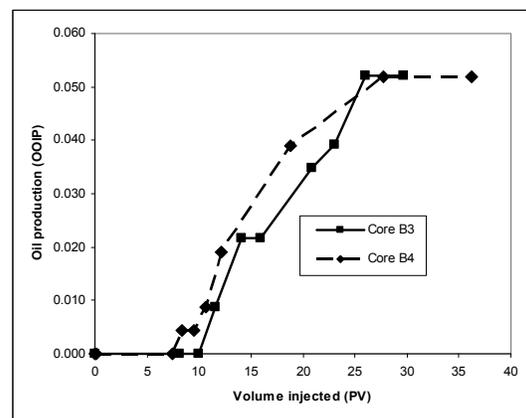


Figure 5. Production profile for GZ-brine flooding Cores B3 and B4