Study the Effect of Alkaline and Surfactants on Improving Iraqi Crude Oil Recovery

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المستخلص

يهدف البحث إلى دراسة تأثير استخدام القلويات والمواد فعالة السطح (مخفضات التوتر السطحي) على تحسين استخلاص النفط الخام العراقي تحت ظروف مختبرية.

أجريت تجارب الإزاحة (الإفاضة) باستخدام محاليل نوعين من المواد القلوية ونوعين من المواد فعالة السطح وبثلاثة تراكيز من كل نوع (0,5 % ، 1% ، 2%) وباستخدام عمود مسامي رملي بطول (8,5 سم) وقطر (6,5 سم) مشبع بالماء العادي ثم شبع بنفط خام البصرة ذو كثافة (40 API^{o}) ولزوجة ديناميكية بحدود (39,6 سنتي بواز) ومقارنة نتائجها مع نتائج استخدام الماء العادي و2% ماء مالح .

التجارب التي استخدم فيها الماء العادي و2% ماء مالح للإزاحة الأولية تم إجراء إزاحة ثانوية عليها باستخدام المواد الكيمياوية بالتراكيز التي أعطت أعلى قيم لمعامل الاستخلاص وأظهرت النتائج زيادة في معامل الاستخلاص الثانوي، وكانت أعلى قيمة لمعامل الاستخلاص 50% باستخدام 0,5% مادة فعالة السطح 2 .

أظهرت نتائج البحث تأثيرات مختلفة لتلك المحاليل على معامل الاستخلاص و بصورة عامة أظهرت المواد القلوية زيادة في معامل الاستخلاص مع زيادة التركيز بينما المواد الفعالة السطح أظهرت انخفاض في هذه القيم بزيادة التركيز. وكذلك أظهرت النتائج إن أعلى قيمة لمعامل الاستخلاص كانت 90,9 باستخدام المادة فعالة السطح 2 وبتركيز 0,5% .

كلمات مفتاحية : الإنتاج المحسن للنفط، الإفاضة بالمواد القلوية، الإفاضة بالمواد الفعالة السطح، معامل الاستخلاص.

Abstract

This research aims to study the effect of using alkaline (caustic) and surfactant materials to imp rove the recovery of Iraqi crude oil under laboratory conditions.

Flooding tests were carried out by using solutions of two alkalines (NaOH, Na_2CO_3) and two anionic surfactants materials were prepared at three concentrations (0.5%, 1%, 2 %) using sand packs with (8.5 cm) length and (6.5 cm) diameter, which is saturated with tap water and then saturated with Basrah crude oil of 40 API° density and 39.5 cp viscosity. The results were compared with the results of flooding tests by tap water and 2wt% brine water.

In tests that tap water and 2wt% brine water were used as a primary recovery a secondary recovery had been tested by using materials that gave highest recovery, the results showed an increase in the recovery and the highest value was 50% by using 0.5% surfactant no.2.

The research showed different effects of these solutions. In general, alkalines type showed an increase in recovery factor vs. concentration, but surfactant type showed decrease in the recovery factor vs. concentration. Also, the results showed that the recovery by using surfactant no.2 were the best respective to other materials, and the highest recovery obtained was 90.9 at 0.5%.

Keywords: Enhanced Oil Recovery, Alkaline flooding, Surfactant Flooding, Recovery Factor

Introduction

In spite of, multiple energy resources, oil will still the main source unchallenged and will remain occupied this position in the coming decades. Recovery is at the heart of oil production from underground reservoirs and the world average recovery factor from hydrocarbon reservoir stick in the mid-30% range.

Primary, secondary and tertiary (enhanced oil recovery EOR) recovery methods follow a natural progression of oil production from the start to a point where it is no longer economical to produce from the hydrocarbon reservoir. The timing of EOR is also important: a case is made that advanced secondary recovery (improved oil recovery or IOR) technologies are a better first option before full-field deployment of EOR [1].

There is a lot of confusion around the usage of the terms EOR and IOR.

Figure (1) shows these terms of oil recovery, as defined by the Society of Petroleum Engineers (SPE)[2,3]. Primary and secondary recovery (conventional recovery) targets mobile oil in the reservoir and tertiary or EOR targets immobile oil (that oil which cannot be produced due to capillary and viscous forces).

Oil industry leaves behind between 60-70% of original oil in place OOIP after primary recovery. Primary and secondary recovery techniques together are able to recover only about 35-50% of oil from the reservoir, this implies that the target for EOR is substantial (2/3 of the resource base)[4]. With the decline in oil discoveries during the last decades it is believed that EOR technologies will play a key role to meet the energy demand in years to come [5].

EOR methods are classified by main mechanisms of oil displacement [5, 6]. There are really just three basic mechanisms for recovering oil from rock other than by water alone. The methods are grouped according to those which rely on (a) A reduction of oil viscosity,(b) The extraction of the oil with a solvent, and (c) The alteration of capillary and viscous forces between the oil, injected fluid, and the rock surface.

EOR methods are therefore classified into the following three categories:

- Thermal methods (injection of heat).
- Miscible gas injection methods (injection of a solvent).
- Chemical methods (injection of chemicals/surfactants).

In chemical EOR or chemical flooding, the primary goal is to recover more oil by either one or a combination of the following processes:

1. Mobility control by adding polymers to reduce the mobility of injected water.
2. Interfacial tension (IFT) reduction by using surfactants, and/or alkalis [1].

Flooding chemicals (surfactant, alkali, alkali-surfactant, and polymer) are not a new technology [7]. In 1956, Reisberg and Doscher [8] proposed that a combination of performed surfactant and alkali could be injected along with water in order to improve recovery of oil. This recovery is generally attributed to the reduction in oil-water interfacial tension in the presence of surfactant. Surfactants are special molecules that are both hydrophobic and hydrophilic, thus the most stable configuration for them is at the interface between oil and water [9, 10].

By arranging themselves in this manner, surfactants can lead to dramatic reduction in the oil-water interfacial tension [9, 11]. It has been shown both experimentally and theoretically [12, 13] that reduction in IFT can lead to an increase in capillary number which can reduce residual oil saturation to a sufficiently low value in the swept regions [14].

Alkali solutions are a special subset of surfactant flooding [15], whereby the injected alkali reacts with naturally occurring organic acids in the oil, leading to the generation of in-situ soaps. The soap molecules also act as surface active agents that may lower the interfacial tension enough to increase production [16].

Existing waterfloods can be rather easily converted to a caustic (alkaline) flood by the addition of (1-5% by weight) alkalis to controll the pH of the injected water to improve recovery beyond that of ordinary waterflooding [17]. The first patent on the use of caustic for enhanced oil recovery was issued to H. Atkinson in 1927[18]. Although caustic (alkaline) flooding appears to be a simple process and relatively inexpensive to apply, the mechanisms involved in displacement of oil are complicated. Johnson [19] suggested that during caustic flooding, four possible mechanisms could occur that will lead to improved oil recovery. Upon reduction of oil-water IFT, oil droplets may become emulsified into the water. The droplets may then be produced along with the water (emulsification & entrainment), or may plug rock pores, leading to improved sweep (emulsification & entrapment). Additionally, rock wettability may alter from water-wet to oil-wet, or oil-wet to water-wet. Wettability alteration will lead to change in oil and water relative permeability [19]. Also, the solubilization of rigid films that may form at the oil-water inter-face will lead to the mobilization of the residual oil. The economics of caustic flooding are appealing because investment for caustic chemicals is relatively low when compared to most other enhanced oil recovery processes [17].
Despite that, production derived from chemical methods at the present time is few compared to other methods, but is expected to increase its importance in the future in the light of the ongoing research to find new materials in a wider range of reservoir conditions as well as improving their economies [4].
Chemical EOR is a very complex technology requiring a high level of expertise and experience to successfully implement in the field but chemical EOR technology is dramatically better than 30 years ago due to more experience, better understanding, better modeling, better enabling technologies and better chemicals at lower cost adjusted for inflation. At current oil prices, oil companies can make a high rate of return using chemical EOR methods [20].

Screening Criteria

Some general criteria were considered in this research according to the literature [17, 20], as follows:

1- Sandstone reservoirs are preferred. Recent laboratory results show performance of surfactant in dolomite reservoir and alkaline in carbonate reservoir just as high as in sandstones.

2- Oil viscosity should be less than 200 cp (light and medium oil), but recent trend is to apply to viscous oils up to 200 cp or even higher viscosity.

3- The acid number of the crude oil should be larger than 0.5 mg KOH/gm of crude.

4- High permeability and porosity.

5- High remaining oil saturation (>25%).

5- Anionic surfactants preferred: petroleum sulfonates and sulfates.

6- Preferred concentration for caustic or alkaline flooding is (1-5% by weight).

7- Preferred pH for alkaline solutions is more than 10.

Methodology

❖ Apparatus

1- Brookfield Viscometer / USA: to measure the dynamic viscosity for the crude oil according to standard specification ASTM D 2196 as shown in figure (2).

2- Electrical balance type Sartorius / Germany.

3- pH meter / Germany: to measure the pH of the alkaline solutions.

Materials

1- Iraqi standard sand provided by State Company for Geological Survey and Minerals. The specifications are shown in table (1).

2- Basra crud oil with density 40^{o} API provided by Al- Dura refinery. Tests were performed to determine crude oil specifications which listed in Table (2).

3- The alkali materials used in this study were: sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH) which available in the lab, its specifications were shown in table (3).

4- The surfactants (detergents) used in this study were commercial anionic surfactants supplied from local market. Specifications are shown in table (4).

❖ Test samples preparation

1- To represent the reservoir cores, 15 sand pack floods with 6.5cm in diameter and 7.5cm in highet were prepared as shown in figure (3).

2- In the bulk liquid experiments, tow qualities of water were investigated: tap water and water containing 2 wt% NaCl. Analyses of tap water were listed in table (5).

3- Solutions of selected chemicals were prepared for flooding tests in three concentrations: (0.5 wt% , 1 wt%, 2 wt%) for alkali materials, and (0.5 vol%, 1 vol%, 2 vol%) for surfactants.

4- pH of the alkaline solutions was measured. The results were listed in table (6).

❖ Experiments

Flooding tests were performed at lab conditions, using the prepared solutions, tap and salt water for comparison, by following the mentioned steps:

1- As a first step, the cores were saturated with tap water.

2- The crude oil then was injected at a constant rate using a volumetric funnel until the cores were at its irreducible water saturation. The displaced water volumes were measured in graduated cylinders and it would be equal to oil volume in place.

3- Cores numbers from (1-12) were flooded with the selected chemicals only.

4- Cores numbers from (13-15) were flooded with tap and salt water followed with chemical flooding for samples that gave best recovery factors.

5- Produced oil volumes were measured using graduated cylinders.

Results and discussion

1- Recovery Factor (RF) was calculated for the cores by the following relation:

Recovery Factor (R %) = Volume of oil displaced / Volume of oil in place

2- For primary flooding tests the recovery factors were calculated. The results are listed in Table (7), shown in figure (4) and diagram (1).

3- Comparison between recovery factor using tap water flooding and other floodings are shown in diagram (2).

4- Comparison between recovery factor using saline water flooding and other floodings are shown in diagram (3).

5- For secondary recovery tests, recovery factors were calculated. The results are listed in table 8and diagram (4).

The results showed that:

1- Increasing in recovery factor values by using alkali materials with increasing of concentration, in the opposite for the surfactant which showed decreasing in these values with increasing of concentration.

2- Sodium carbonate (Na_2CO_3) gave better results than sodium hydroxide (NaOH) with increasing concentration; high recovery factor value was 83.7% at 2 wt% Na_2CO_3.

3- Surfactant type 2 gave better results than type 1and the high recovery factor was 90.9% at 0.5 vol% concentration.

4- Recovery by saline water (2 wt %) gave higher results than tap water by 6%.

5- Recovery by tap water was better than alkalis at certain concentrations, except sodium carbonate material at 1 wt% and 2 wt% which the values were higher by 3.5% and 7.7% relatively.

6- Recovery by saline water was better than selected chemical materials except sodium carbonate at 2 wt% and surfactant type 2 at 0.5 vol%.

7- Surfactant type 1 gave the lower recovery factor values at all concentrations.

8- Increasing oil recovery ratios in secondary flooding tests and the highest value was carried out by using surfactant type 2 at concentration 0.5 vol%, and the lowest was by using sodium hydroxide at concentration 2 wt%.

Conclusions

A suite of bulk liquid and core flooding experiments has been performed to study the effects of alkaline and surfactant flooding on Iraqi crude oil recovery.

We observed that, primary alkaline and surfactant floods are not significantly more efficient than water floods (tap and saline water), so the economical factor will play role in selected waterflooding as primary recovery.

After water flooding, it is better to use chemical flooding as secondary recovery to recover more oil due to emulsification and entrapment of oil droplets which is the mechanism responsible for oil recovery.

It was determined from recovery experiments that surfactant was not sufficient to emulsify oil, but it did result in increased water-wetting of glass, and the type and structure of surfactant has a big effect on their recovery efficiency.

Sodium carbonate (Na_2CO_3) showed better results than sodium hydroxide (NaOH) because of its buffering capabilities and because it tends to lead greater reduction in oil-water interfacial tension.

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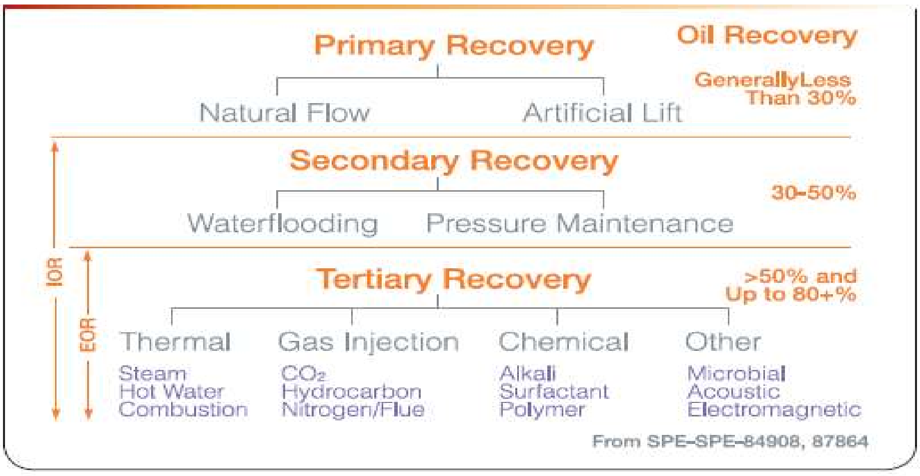


Fig. (1) EOR / IOR definition

Fig. (2) Brookfield Viscometer

Table (1) Specification of Iraqi standard sand

Weight loss after acid wash%	Pass from sieve 0.850 mm	Pass from sieve 0.600 mm	SiO_2 %
0.25 Max	98 Min	10 max	97 Min

Table (2) Specification of Basra crude oil

Density (gm/cm^3)	Kinematic viscosity (cp)	Acid No. (mg KOH / gm of crude)
0.8251	39.6	2.49

Table (3) Specification of chemical materials

Formula	Mol. wt. g/mol	Grade	Sp. Gr. g/cm^3	Solubility in water @ 20^oC g/100ml
NaOH	40	Flake	2.13	111
Na_2CO_3	106	Pellets	2.53	21.5
NaCl	58.4	powder	2.16	36

Table (4) Specification of surfactant (detergent) materials

Type 1	Al-wazir company for detergent / Syrian company	Anionic active material 30%
Type 2	Modern industries company/ Saudi company	Anionic active material 15-30% , Nonionic active material 5-15%

Table (5) Specification of tap water

PH	Turbidity	Electrical conductivity (µs/cm)	Total dissolved solid (TDS) (ppm)	Total hardness (T.H.)	Ca^{+2}	HCO_3^-	Na^{+1}
8	7.2	998	520	420	160	183	45.7

Table (6) pH values of alkaline solutions

Alkaline Material	Concentration (%)	Temperature(^oC)	PH
Na_2CO_3	0.5	27.5	10.57
	1	26.7	10.63
	2	26.6	10.56
NaOH	0.5	26.9	12.46
	1	26.8	12.34
	2	26.6	12.18

Fig. (3) Recovery test system

Table (7) Values of recovery factor

Core No.	Type and concentration of material	Displaced Oil Volume (cm^3)	Original Oil in place (cm^3)	Recovery Factor (R%)
1	0.5 wt% sodium hydroxide	53	73	72.6
2	1wt% sodium hydroxide	72	96	75
3	2wt% sodium hydroxide	63	82	76.8
4	0.5 wt% sodium carbonate	58	80	72.5
5	1wt% sodium carbonate	70	88	79.5
6	2wt% sodium carbonate	72	86	83.7
7	0.5 vol% surfactant 1	64	96	66.7
8	1 vol% surfactant 1	58	95	61
9	2 vol% surfactant 1	54	96	58.7
10	0.5 vol% surfactant 2	80	88	90.9
11	1 vol% surfactant 2	77	96	80.2
12	2 vol% surfactant 2	66	95	69.5
13	Tap water	70	92	76
14	Tap water	70	92	76
15	2 wt% saline water	69	84	82

Table (8) Values of recovery factor after secondary recovery

Core NO.	Type of Primary Recovery	Primary Recovery Factor (R%)	Type of Secondary Recovery	Oil Recovered after Secondary Recovery (cm^3)	Original Oil in Place (cm^3)	Secondary Recovery Factor (R%)
13	Tap water	76	0.5 vol% surfactant 2	11	22	50
14	Tap water	76	2 wt% sodium hydroxide	5	22	22.7
15	2 wt% saline water	82	2 wt% sodium carbonate	5	15	33

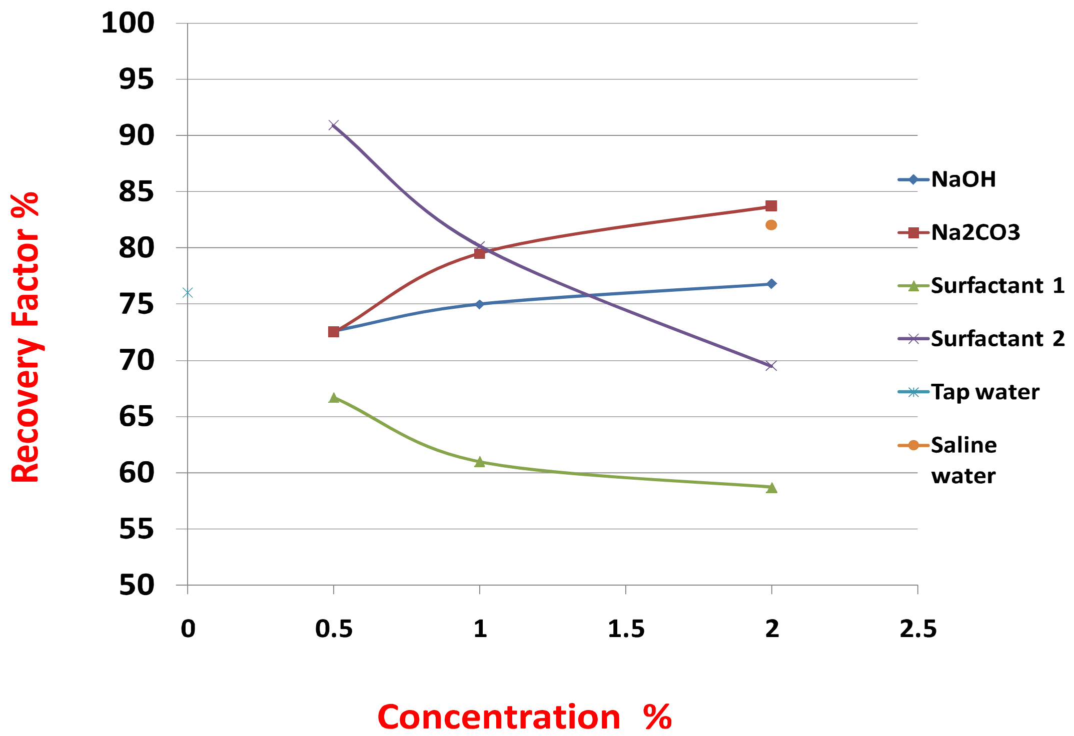
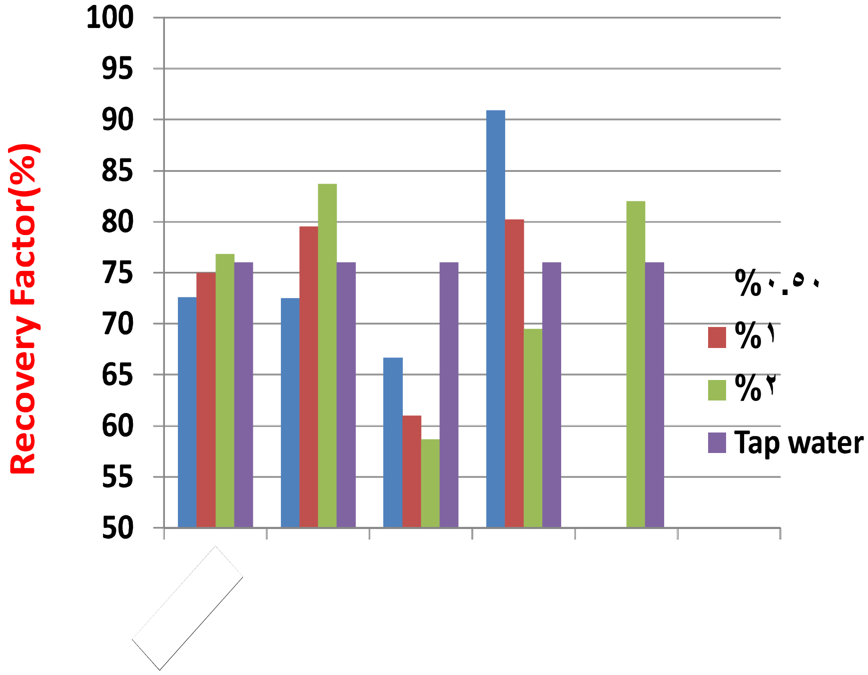
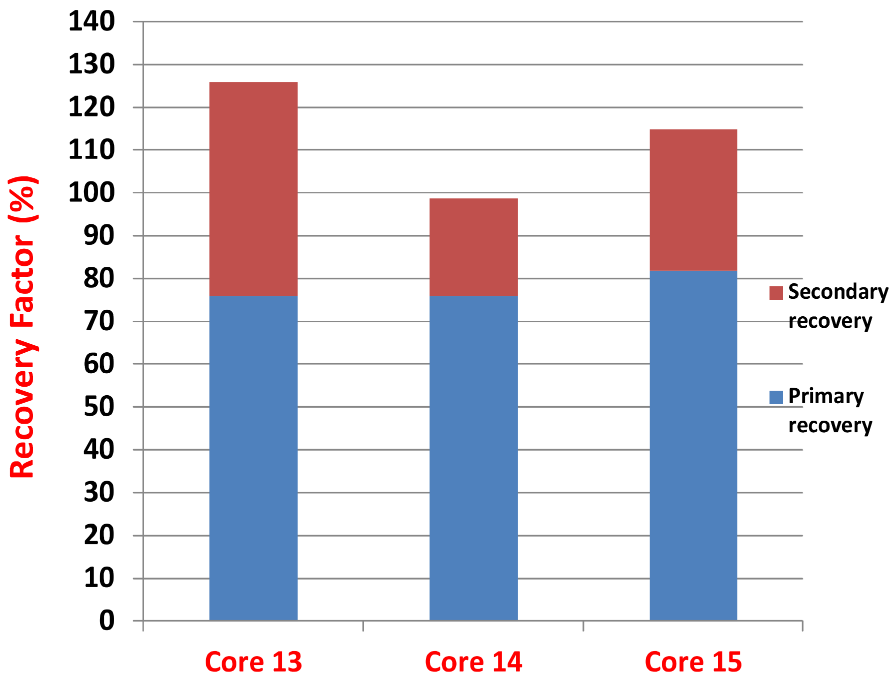


Fig. (4) Values of Recovery Factor vs. Concentration



Recovery Factor(%)
100
95
90
85
80
75
70
65
60
55
50
%۰.۵۰
%۱
%۲
Tap water


Recovery Factor (%)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Core 13
Core 14
Core 15
Secondary recovery
Primary recovery