Dissolving Precipitated Asphaltenes Inside Oil Reservoirs Using Local Solvents

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Abstract

There are several oil reservoirs that had severe from a sudden or gradual decline in their production due to asphaltene precipitation inside these reservoirs. Asphaltene deposition inside oil reservoirs causes damage for permeability and skin factor, wettability alteration of a reservoir, greater drawdown pressure. These adverse changing lead to flow rate reduction, so the economic profit will drop. The aim of this study is using local solvents: reformate, heavy-naphtha and binary of them for dissolving precipitated asphaltene inside the oil reservoir. Three samples of the sand pack had been prepared and mixed with a certain amount of asphaltene. Permeability of these samples calculated before and after mixed with asphaltenes. Then, the permeability of samples calculated after solvents injection into that porous media. After that, all the values of samples permeability converted to average permeability damage compared with the pure samples. The results show the average permeability damage of samples that mixed with 20 gm was 24 %, but after reformate injected reduced to 14 %. After injected heavy naphtha to porous media, the average permeability reduced only to 17%. The binary solvent had been prepared from reformatted mixed with heavy naphtha gained the best results because it dropped the average permeability damage to 10%.

Keywords: asphaltene deposition, Iraqi local solvents, permeability damage, oil reservoirs, reformates heavy naphtha.

Received on 04/09/2019, Accepted on 01/11/2019, published on 30/03/2020

https://doi.org/10.31699/IJCPE.2020.1.7

1- Introduction

This decrease in permeability within the reservoir is called formation damage. There are many types of formation damage that are mainly divided into organically produced by chemical reactions between the rock and fluids or fluids among them, either the second type is mechanical which arises due to production or drilling operations due to force and movement[1].

There are many ways to increase permeability, including acidicizing of the layer by injecting organic acids such as Hydrochloric Acid (HCl) and Hydrofluoric acid (HF) into the layer for scrubbing pore surfaces and thus increase permeability. Another method is hydraulic fracturing, which is done through high-pressure liquid injection to reservoir formation and as a result, the permeability increases [2].

One of the serious damage cases is the deposition of asphaltenes inside the reservoir that generate organic damage to permeability. Asphaltenes deposition probably occurs inside the reservoir or inside the production pipes or in the surface facilities. For the purpose of removing the asphaltenes inside the reservoir, a solvent such as toluene or benzene is injected for dissolving it in the pores and thus restore the unaffected permeability [3].

It is worth noting that the problem of asphaltenes is a global problem that occurs in both light and heavy oil reservoirs.

This problem has caused a huge economic loss because it is working to significantly reduce oil production. Many of the Iraqi fields suffer from this issue, as happens in the Bazargan field and the East Baghdad field.

The main reason for the possible deposition of asphaltene is the chemical composition of the oil. So to know the stability of asphaltene in crude oil must know the compounds of crude oil. The percentage of saturated, resin, aromatic and asphaltene compounds that presence in the crude oil then analyzed these compounds by a process called SARA analysis. Oil components either measure by ASTM test or by nuclear magnetic resonance (NMR). Crude oil components: saturates, resins, aromatics, and asphaltenes can be predicted by nuclear magnetic resonance by measuring aromatic hydrogen and aromatic carbon for crude oil. SARA analysis is an analytical method for the crude oil components by which the stability of the asphaltene is revealed. This method includes calculating the values of certain variables and these variables reflect the stability of crude oil [4], [5].

Four types of damage are caused by the formation of asphaltenes inside the porous media [6]:

- Reduce permeability.
- Change of wettability.
- The decrease in viscosity of crude oil.
- Formation of water emulsions in oil.
1.1. Permeability Measurements

Permeability is the property of the porous medium that dealing with the capacity and capability of the formation to conduct fluids flow. It director directional movement and flow rate of fluid flow [7]. Darcy developed equation represented the fluid flow through a porous medium and it became one of the most popular equations in reservoir engineering. This equation found in many forms, one of them the following formula for horizontal linear incompressible flow through a porous medium [8]:

\[
Q = A \times \frac{k}{\mu} \times \frac{\Delta P}{L}
\]

(1)

There are many assumptions to the above equation includes [8]:
- The direction of flow is horizontal.
- The regime of flow is laminar.
- There is a fluid in a porous medium.
- Between rock and fluid should not be a chemical process.

Reservoir rock with a high value of permeability leads to produce a large amount of commercial oil and gas for a long period. In contrast, reservoir rock with low permeability may not able to produce a large quantity of oil and gas. Because one Darcy is a very high value for reservoir rock, milliDarcy is a more common unit in permeability calculation [7]. Worthwhile, The relationship between core and well log data was determined by Artificial Neural Network (ANN) in cored wells to develop the predictive model and then was used to develop the flow unit prediction to un-cored wells [9].

There are factors affecting permeability values [10]:
- Shape and size of sand grain: Rock with small flat grains has less permeability from the rock with the large rounded grain.
- Lamination: rock with shale lamination has less permeability than layers without lamination.
- Cementation: porosity and permeability affected by the type and position of cementation within the rock.

The permeability of rock describe according to Table 1:

| Permeability range, mD | Permeability description |
|-----------------------|-------------------------|
| 1 < k                 | Poor                    |
| 1 < k < 10            | Fair                    |
| 10 < k < 50           | Moderate                |
| 50 < k < 250          | Good                    |
| 250 < k               | Very good               |

There are too many sources of permeability data include [12]:
- Core sample laboratory measurement.
- Nuclear magnetic response (NMR).
- Drill stem test and other well pressure tests.
- Well logging with indirect methods.
- Correlations that attempt to forecast permeability from porosity values.
- Geostatistical techniques attempt to predict permeability with spatial variation.

2- Experimental Work

2.1. Materials

a. Crude Oil

The physical oil properties of crude oil from Tannumah illustrated in Table 2 after provided from Midland Oil Company

| Property                  | Value   |
|---------------------------|---------|
| Specific gravity          | 0.922   |
| API gravity               | 22      |
| Viscosity at 37 C, cP     | 31      |
| Saturate compounds, % wt. | 42.3    |
| Aromatic compounds, % wt. | 26.7    |
| Resin compounds, % wt.    | 18.2    |
| Asphaltene compounds, % wt. | 12.8    |

b. Toluene

According to (HSDB, 1991) “Toluene is a combustible, colorless, anticorrosive fluid as the same as benzene odor”. It is unsolvable in water and solvable in acetone, absolute alcohol, ether, chloroform, benzene, petroleum ether, glacial acetic acid, and carbon disulfide). Toluene's molecular formula is C7H8.

c. Hexane

The n-hexane used in these experiments had been gotten from AL-Dura Refinery. Hexane represents a precipitant liquid for asphaltene. It used to illustrate the effect of solvent in reduced asphaltene deposition. The molecular formula of hexane is C6H14.

d. Reformate

Reformate is a solvent liquid for asphaltene. Reformate had been gotten from AL-Dura Refinery. The properties of reformate that used in this study shown in Table 3.

Table 1. Description of permeability values [11]

Table 2. Physical oil properties of a sample
Table 3. Properties of reformate

| API  | 61.7 |
|------|------|
| Specific gravity at 60°F/60°F | 0.733 |
| Sulfur Content | 3 ppm |
| ASTM distillation | Boiling point(C°) |
| The distillate, vol% | |
| 60 | IBP |
| 88 | 10 |
| 94 | 20 |
| 106 | 30 |
| 110 | 40 |
| 117 | 50 |
| 124 | 60 |
| 132 | 70 |
| 140 | 80 |
| 147 | 90 |
| 178 | FB |

This study building on a simple system consists of the reservoir tank, core holder, water bath and Co2 bottle.

a. Reservoir tank and accessories

A container tank has been made from the carbon steel layer (5 mm thickness) in order to resist high pressures.

All the joints tools manufactured from Tungsten so as to bear the high pressures.

That apparatus holds two orifices, the first on the roof of the container with a gate valve (inlet) to fill up the tank by either oil, water or solvents, the other passageway to transfer the fluids to the core holder.

b. Core holder

Core Holder is composed of a high-pressure tube that has 1.5” an internal diameter.

It connects with the container tank from side and tape from the other side.

As well it is made up of a pipe that has an external diameter of 1.5” (38 mm) and an internal diameter of (30 mm), it manufactured of anti-corrosion stainless steel to prevent corrosion error. Besides, it provided with very fine filter bond inner the pipe to stop of sand pack movement or sand grains along the pipes.

c. CO2 bottle

A Co2 2000 psi bottle has been used through the experiments to move fluids into the sand pack

d. Check valve

The check valve has been used to push the fluid forward only and pressurized the contained fluid.

e. Heater

Used for heating the injected fluids through the system. it put on the route vessel. That vessel bearing a high boiling point has been placed over this heater.

f. Pressure Differential Gauge

Used for measuring the pressure drop along with the sand pack with upper limit reading 3000 psi.

g. Thermometer

A thermometer is a tool that measures temperature or a temperature gradient.

The fluid injection system and its part illustrated in Fig. 1, Fig. 2 and Fig. 3.

e. Heavy Naphtha

Heavy Naphtha is a solvent liquid for asphaltenes. Reformate had been gotten from AL-Dura Refinery. The properties of reformate that used in this study shown in Table 4.

Table 4. Properties of heavy naphtha

| API  | 54.9 |
|------|------|
| Specific gravity at 60°F/60°F | 0.759 |
| Boiling range(C°) | (90 – 180) C |
| BTX content, vol% | |
| Benzene | 3.18 |
| Toluene | 14.94 |
| P and M xylene | 17.66 |
| O-xylene | 11.58 |
| ASTM distillation | Boiling point(C°) |
| The distillate, vol% | |
| 43 | IBP |
| 71 | 10 |
| 80 | 20 |
| 86 | 30 |
| 92 | 40 |
| 97 | 50 |
| 103 | 60 |
| 110 | 70 |
| 121 | 80 |
| 144 | 90 |
| 154 | 95 |
| 180 | FB |

Nanotechnology has shown a lot of promise in the oil and gas sectors, including nanoparticle-based drilling fluids [13]. So, the Nano surfactant materials recommended for use.

2.2. Sand

Sand has been used to make the sand packing with magnitude scattering of 80 to 500 µm.

2.3 Fluid injection system

All the experiments related to testing flow rate and pressure through the core sample needed to the fluid injection system. The accuracy of that system is too sensitive. So, the price of an accurate system reaches to 500,000$. 

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2.4. The Procedure of the Fluid Injection Experiment

a. The Preparation of Sand Pack

Sand granules with sizes between 80 and 500 are washed and dried. In some cases the sand mixed with a certain weight from asphaltene to reduce permeability and shown the effect of asphaltene on permeability calculations, then placed inside the tube ends with a filter from both sides to prevent sand leaking out and allowing the fluid to pass into and out of the tube.

b. The Preparation of Injected Fluid

The crude oil with or without solvents were injected to sand pack for showing the permeability changes that occurred due to the presence of solvents. The stirrer device has been used to make homogenously mixed fluid.

c. Permeability measurements

Using Darcy’s Law, the permeability of the sand pack in different cases has been calculated. The equation of Darcy’s law shown below:

\[ Q = A \times \frac{\mu}{\mu'} \times \frac{\Delta P}{L} \]  

**Table 5. Darcy’s equation input**

| parameter                        | value | unit   |
|----------------------------------|-------|--------|
| Cross sectional area            | 7.068 | cm²    |
| Length of the core holder        | 10    | cm     |
| Viscosity of water               | 1     | cP     |
| Viscosity of oil                 | 31    | cP     |
| The viscosity of oil-reformate    | 28.34 | cP     |
| mixture                          |       |        |
| The viscosity of oil-heavy naphtha | 26.61 | cP     |
| mixture                          |       |        |
| The viscosity of oil-reformate-heavy naphtha mixture | 27.21 | cP |

3- Results and Discussion

3.1. 3.1. Permeability

Asphaltenes represent the cholesterol of petroleum engineering because it blocks the passageway of movable oil. It adversely affects the permeability property of rocks, no doubt lead to production reduction. To illustrate the effect of asphaltene and solvents that injection for asphaltene dissolving must measure the original permeability, the damaged permeability, and the recovered permeability. The study depends on eleven different cases for the illustration of its goal.
These cases are shown in Table 6. In each case, the sand pack fully saturated with injection liquid for 1 hour for precipitant or dissolve asphaltene then reinjection the same liquid for permeability measurement purposes.

Table 6. Cases of permeability measurements

| Case number | Rock state | Injection fluids |
|-------------|------------|------------------|
| 1           | Sands      | water            |
| 2           | Sand + 20 gm Asphaltene | Oil          |
| 3           | Sand + 20 gm Asphaltene | Crude oil 80 % + n-hexane 20 % |
| 4           | Sand + 20 gm Asphaltene | Crude oil 80% + reformate 20 % |
| 5           | Sand + 20 gm Asphaltene | Crude oil 80 % + heavy naphtha 20 % |
| 6           | Sand + 20 gm Asphaltene | Crude oil 80 % + heavy naphtha 10 % + reformate 10 % |

a. Case 1

Using the injection system, the permeability of three pure sand packs calculated. Pressing crude oil that presence in container tank by co2 bottle stimulates the oil to enter the core holder. Measure the pressure in inlet and outlet give differential pressure. Measure the volume and time given flow rate. The results are shown in Table 7.

The difference in permeability between three sand pack samples belongs to the difference in flow rate and pressure drop. The last difference result from the unlike composite of each simple

Table 7. Permeability calculations of case 1

| sample | V (cm^3) | t (sec.) | Q (cm^3/sec) | (cm^3/sec)/(cP)/sec | atm. | atm./cm | Darcy |
|--------|----------|----------|--------------|---------------------|------|---------|-------|
| 1      | 33.2     | 10       | 3.32         | 0.47                | 4.2  | 0.42    | 1.123 |
| 2      | 33.8     | 10       | 3.39         | 0.48                | 4.7  | 0.47    | 1.027 |
| 3      | 32.5     | 10       | 3.25         | 0.46                | 5.2  | 0.52    | 0.89  |

b. Case 2

To illustrate the effect of asphaltene precipitated on permeability, the sand pack sample mixed with 20 gm of dry asphalt. The results are shown in Table 8.

The average permeability damage was 24 % that means a quarter of well production performance declined. It calculated from this equation:

average permeability damage (APD) = \frac{\sum_{i=1}^{n} \text{permeability damage (APD) of each sample}}{n} (2)

Table 8. Permeability calculations of case 2

| Sample | V (cm^3) | t (sec.) | Q (cm^3/sec) | (cm^3/sec)/(cP)/sec | atm. | atm./cm | Darcy |
|--------|----------|----------|--------------|---------------------|------|---------|-------|
| 1      | 16       | 60       | 0.27         | 1.18                | 13.6 | 1.36    | 0.868 |
| 2      | 16       | 60       | 0.27         | 1.18                | 15.5 | 1.55    | 0.764 |
| 3      | 15       | 60       | 0.25         | 1.09                | 16.8 | 1.68    | 0.651 |

c. Case 3

To illustrate the effect of n-hexane (precipitant) on crude oil, case 4 includes mixed 80 % crude oil and 20 % n-hexane. Also, sand packs mixed with 20 gm dry asphaltene. The results are shown in the 9 with 48% average permeability reduction. That means almost half of the production performance dropped.

d. Case 4

Sand pack mixed with 20 gm of dry asphalt. Also crude oil in this case mixed with reformates solvent (80 % wt. crude oil + 20 % wt. solvent). The results are shown in Table 10. The average production damage was 14 %. That means only 14 % of production performance declined, while in case two was 24 % that similar to this case apart from fluids there is only crude oil without solvent.

Table 9. Permeability calculations of case 3

| sample | V (cm^3) | t (sec.) | Q (cm^3/sec) | (cm^3/sec)/(cP)/sec | atm. | atm./cm | Darcy |
|--------|----------|----------|--------------|---------------------|------|---------|-------|
| 1      | 15       | 60       | 0.25         | 1.09                | 17.1 | 1.71    | 0.64  |
| 2      | 12.5     | 60       | 0.2          | 0.87                | 17.5 | 1.75    | 0.5   |
| 3      | 12.5     | 60       | 0.2          | 0.87                | 20   | 2       | 0.437 |

e. Case 5

Another solvent used to remove the asphaltene particle is heavy naphtha. In this case, mixed of 80 % crude and 20 %, heavy naphtha injected to sand packs mixed with 20 gm of dry asphalt.

The results of this experiment were shown in Table 11. The average permeability damage was 17 %. That means only 17 % of production performance declined,
while in case two was 24 % that similar to this case excluding for fluids, there is only crude oil without solvent.

Table 11. Permeability calculations of case 5

| Sample No. | V (cm³/sec) | t (sec) | Q (cm³/sec) | q × μ (cm² atm/~sec cm cP) | ΔP (atm) | ΔP/L atm/cm | k (Darcy) |
|------------|------------|--------|-------------|--------------------------|---------|------------|-----------|
| 1          | 11.1       | 60     | 0.185       | 0.7                      | 8.3     | 0.83       | 0.844     |
| 2          | 12         | 60     | 0.2         | 0.75                     | 8.9     | 0.89       | 0.844     |
| 3          | 12         | 60     | 0.2         | 0.79                     | 9.7     | 0.97       | 0.818     |

f. Case 6

Binary solvent from 10 % heavy naphtha and 10 % reformate was prepared and mixed with 80 % crude oil. Sand packs also mixed with 20 gm dry asphalt. The results of these experiments were shown in Table 12. The average permeability damage was 10 %. That means only 10 % of production performance dropped, whereas, in situation two was 24 % that similar to this situation with the exception of fluids, there is only crude oil without solvent.

Table 12. Permeability calculations of case 6

| Sample No. | V (cm³/sec) | t (sec) | Q (cm³/sec) | q × μ (cm² atm/~sec cm cP) | ΔP (atm) | ΔP/L atm/cm | k (Darcy) |
|------------|------------|--------|-------------|--------------------------|---------|------------|-----------|
| 1          | 10.8       | 60     | 0.18        | 0.68                     | 7.2     | 0.72       | 0.948     |
| 2          | 12         | 60     | 0.2         | 0.78                     | 8.5     | 0.85       | 0.917     |
| 3          | 12         | 60     | 0.2         | 0.78                     | 9       | 0.9        | 0.872     |

3.2. Average Permeability Damage

After measure permeability damage in each case compares it with initial permeability using the equation. The higher average permeability damage means higher production performance damage. The results are shown in Table 13 and in Fig. 4.

Table 13. Summary of average permeability damage

| Case No. | Average Permeability Damage |
|----------|-----------------------------|
| 2        | 24                          |
| 4        | 48                          |
| 6        | 14                          |
| 8        | 17                          |
| 10       | 10                          |

From figure these points are observed:
- The first five values represent the higher permeability damage due to the absence of the solvents within the sand packs.
- Presence n-hexane in 4 and 5 cases gave more average permeability damage than other cases due to the precipitant characteristics of n-hexane.
- The effectiveness of the solvents used in the study in preventing and dissolving the asphaltenes according to the preference as follows:

\[
\text{Binary heavy naphtha} \rightarrow \text{reformate} \rightarrow \text{Heavy naphtha} \rightarrow \text{Reformate}
\]

4- Conclusions

a. Solvent quality order in preventing the deposition of the asphaltenes, respectively: binary of reformate-heavy naphtha, then reformate, the less profitable was heavy naphtha.
b. Solvents have a great influence to reduce average permeability damage. Solvents dissolve the asphaltene that leads to minimizing the advertising effect of asphaltenes.

Recommendation

a. Using real cores and plugs damaged with asphaltenes instead of using the sand pack. The cores and plugs prefer to be different types of reservoir rock such as sandstone and limestone.
b. Working an economical model for real field case for knowing the optimization quantity and types of solvent required for injection.
c. Working on an accurate fluid injection system from a global company consists of digital meters and a piston pump.

Acknowledgments

I would like to thank my supervisor Assist Prof. Dr. Faleh H. M. Almahdawi for his kindness and forgiveness in a critical stage in this study. Furthermore, all his care and advice contributed to all the good work in this study.
Nomenclature

\( \Delta P \) pressure drop, atm.
\( \mu \) viscosity, (cP)
A cross-sectional area, cm\(^2\).
ASTM American Society for Testing and Materials
BTX benzene, toluene and xylene
HCL hydrochloric
HF hydrofluoric
K permeability, Darcy.
L length of the core sample, cm.
Q flow rate, cm/s.

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أذابة الاسفلت المتسبب داخل المكامن النفطية باستخدام مذيبات محلية

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الخلاصة

هناك العديد من المكامن النفطية التي تعاني من فقدان تدريجي أو مفاجئ للإنتاج بسبب ترسب الأسفلت داخل تلك المكامن. ترسب الأسفلت داخل المكامن النفطية يؤدي إلى التضرر الronymي وتغيير التدليك المكمني. وزيادة فقدان الضغط وكل هذا يؤدي إلى انخفاض قيم الإنتاج وبالتالي انخفاض القيمة الاقتصادية للمشروع. الألدة من هذه الدراسة هو استخدام مذيبات محلية لأذابة ترسبات الأسفلت داخل المكامن النفطية. ثلاث أنواع من المذيبات المحلية اخترت وهي النفثة الثقيلة والريفورميت ومزيج محدد منهما. ثلاث نماذج حضرت من الرمل بيئة صخور وتم تثبيتها مع وزن محدد من الأسفلت. قيم النفاذية لهذه النماذج حسبت قبل وبعد المزج وبعد حقنها بالمذيبات المحضرة. كل قيم النفاذية تم تحويلها إلى معدل التضرر الronymي مقارنة مع النموذج الأصلي غير الملسو. النتائج اظهرت حدوث تضرر طبيعية مع معدل 24% عند مزج النموذج مع 20 غم من الأسفلت. وهذا الحد المعافض على 15%، 17% 10% بعد حقن الريفورميت والنفثة الثقيلة والملسو منهما على التوالي.

الكلمات الدالة: ترسب الأسفلت، المذيبات المحلية العراقية، تضرر النفاذي، المكماة النفطية، الريفورميت، النفثة الثقيلة.