Discover of GWLI as chemical flooding using SIT: experiment and analysis on key influence factor for oil recovery improvement

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Abstract. Spontaneous Imbibition Test (SIT) is regarded as an important mechanism of oil recovery by water-flood, particularly in heterogeneous or fractured reservoirs where direct displacement of oil by water is usually poor. In this paper a new chemical technology (i.e. Gaberoun Water Lake Injection (GWLI)) has been discovered. It has several advantages which are relatively cheap and reliable. It potentially would have a wide range of applications in brine injection such as altering the rock wettability and responsible for increased ultimate recovery. Two stages of GWLI were discussed with changing pH and salinity. The first stage was used the core samples from carbonate and sandstone, which aged in oil for long time period. The second stage was used the core samples, which aged in oil for short time period. SIT was performed at 27, 30, 40, 50, 60 and 70°C with sandstone and carbonate rock with different aging time. The result showed that the oil recovery was decreased with a decrease in pH values and increased with a decrease salinity. However, the oil recovery in the long aging process was low comparing to the short aging process. The findings in this research that GWLI can be used for oil recovery processes.

Keywords: Gaberoun Water Lake Injection; Salinity; pH; Carbonate; Sandstone; Oil recovery, Aging time; Temperature; Spontaneous imbibition test.

1. Introduction
Improving oil recovery is recognized as the major target and challenge at the different stages of an oil field development. Among several methods in oil recovery, Injection of water into the reservoir is the usual the way to push the oil in front of the water towards the production well ([2]; [8]). Much oil remains in carbonate and sandstone oil reservoirs after water-flood and in some cases in paleotransition zones, which result from the oil/water contact moving upward before discovery [13]. At this point, a high remaining oil saturation is left in reservoir, mainly because of wettability conditions, fractures, layers with large permeability contrasts, impermeable layers during imbibition. Capillary imbibition is described as a spontaneous penetration of a wetting phase into a porous media while displacing a non-wetting phase by means of capillary pressure, e.g., Water imbibes into an oil-saturated rock. It has been stated that the rate of imbibition increased with an increase in temperature due to reduction of oil-water interfacial tension, oil viscosity and water viscosity [[9]. It is clear that the crude oil-brine-rock interactions are responsible for the dramatic increase in oil recovery with
temperature increase rather than changes related to the rock properties alone [11]. Another study is performed by using a similar chalk core sample and the results were comparable. Changes in temperature, using refined oil are not verified in this study [7].

The effect of temperature on oil recovery is the oil production rate increase or decrease with temperature, the studies shows that the temperatures has an important factor in increasing the cumulative oil recovery ([14]; [15]). Therefore the decrease in the viscosity ratio of oil and water due to increasing temperature result in oil being displaced more easily and the ultimate recovery being improved [3]. The time factor for equilibration has long been considered in restoring the original wetting condition of reservoir core samples. The length of time required to incubate the core samples, however, varies from one laboratory to another, ranging from a few days to months ([4]; [10]; [5]; [6]; [12]). A number of research works have been published in effect of hardness on oil recovery indicating that calcium ion Ca$^{2+}$, magnesium ion Mg$^{2+}$, and sulfate ion SO$_4^{2-}$ in brine injection process. Both the concentration of Ca$^{2+}$and SO$_4^{2-}$ at the carbonate surface increases as the temperature is increased. As Mg$^{2+}$ is even able to displace Ca$^{2+}$ from the carbonate rock at high temperature, it should also be able to displace the Ca$^{2+}$ carboxylate complex from the surface. Investigation of effect of brine concentration on oil recovery often showed a significant increase in laboratory water-flood recoveries with a decrease in salinity for duplicate outcrop core plugs [16]. In this study was done to study the effect of pH and salinity on oil recovery by GWLI. The objective of this study to study the effect of GWLI on the oil recovery on sandstone and carbonate reservoirs at different temperature. To study the effect of change pH and the salinity on oil recovery.

2. Materials and Equipment

Figure 1 and 2 shows 12 cores of sandstone and 12 cores of carbonate from wells in the south of Libya were used. Oil sample used in this study with density of 0.764123 g/c.c and GWLI from Gaberoun Lake in Awbari desert. Ethylene Diamine Tetra Acetic Acid, E.D.T.A, was used to determine amount of calcium and magnesium in GWLI. pH=10 organizer solution was used determine amount of calcium and magnesium in GWLI. EBT Guider powder and Murexide Guider Powder were used as indicator to determine amount of calcium in GWLI. Sodium hydroxide solution, sodium chloride, toluene, barium chloride, conditioning agent was used in determine of sulfate concentration in GWLI.

Figure 1. Carbonate cores that used In this study Figure 2. Sandstone cores that used in this study.

SIT was conducted in test tubes as shown in Figure 3. Soxhcelate Extractor Device was used in the process of cleaning core sample from oil. A pH meter, Spectrometer Device, Flame Photometer Device and Burette Bearer is used to measurement of properties of GWLI. Figure 4 shows Vacuum Chamber is used to saturate cores with distillate water and oil.

3. Methodology

The following three steps are used in the procedure for preparing and doing experiment. They are shown in Figure 5 and described in detail as follows.

1. GWLI analysis and preparation
2. Core sample preparation
3. Spontaneous imbibition test
   - Put the saturated core sample with oil in spontaneous imbibition pipes.
   - Fill spontaneous imbibition pipes that consist core sample by GWLI as showing in figure 8.
   - Close the pipe orifice by using aluminum foil and paper tape to prevent the oil from evaporation and left at room temperature until equilibrium is reached.
   - After the equilibrium is reached, the volume of the displacing oil is measured.
   - Then, raise the oven temperature to 30°C to displacing oil out of the sample until equilibrium is reached, the volume of the displacing oil is measured.
   - Repeat the PIT with raising the temperature to 40°C, 50°C, 60°C, and 70°C to displacing oil out of the sample until equilibrium is reached, the volume of the displacing oil is measured.

Figure 3. test tubes that used in this study  Figure 4. Vacuum Chamber that used in this study.
4. Results and Discussion

4.1 GWLI Analyses Results

The average pH value of GWLI is 11.11, the conductivity is 173.5 ms/cm, the salinity is 1.7 ppt, and acidity of GWLI is 0.00235. The densities of GWLI is 1.089 g/ml and distillate water is 0.998 g/ml. The average consuming volume of EDTA solution is 0.375, calcium is 15 mg/l, and the magnesium is 49.8 mg/ L. Table 1 showed the concentration of sulphite (SO₄) in GWLI with change in salinity and pH. The porosity is range from 27% to 14% for carbonate rocks, while it is range from was 31% to 23% for sandstone rocks.
Figure 6. Vacuum system.

Figure 7. Baker in oven

Table 1. Sulfate concentration result

| Sample GWLI          | Y(ABS)  | X       |
|----------------------|---------|---------|
| Origin GWLI without change | 1.004   | 91.41667 |
| GWLI with salinity 23 | 1.84    | 2094.083 |
| GWLI with salinity 10 | 4.055   | 3802.333 |
| GWLI with pH 7        | 7.52    | 634.4167 |
| GWLI with pH 4        | 0.277   | 1541.667 |

Figure 8. Close pipe orifice to prevent evaporation of oil

4.2 Results of Spontaneous Imbibition Test

4.2.1 Results of Carbonate core samples that aged in oil for long time period. Figure 9 shows three carbonate core samples (C211, C212, and C213) with pH is 11.17 and salinity is 170 ppt. At 71:55 hours, cumulative oil recovery at room temperature was reached at (2.24%, 19.84%, 5.11%), respectively. The cumulative oil recovery continues increasing at different temperature until reach maximum recovery with 70°C and 817:45hr to (53.94%, 53.44%, 51.13%), respectively.

Figure 10 shows carbonate cores (C210 and C214) that imbibition by GWLI at pH=7 and C413 at pH=4 and salinity is 170 ppt. The cumulative oil recovery at room temperature was stable at (0.89%, 9.20%), respectively. The cumulative oil recovery increases gradually with increase the time and temperature until at 70°C to (34.05%, 57.09%) for (C210, C214).

4.2.2 Sandstone core samples that aged in oil for long time period. Figure 12 shows sandstone core samples (S105, S115, S102), that aged in oil to nearly one year. SIT used with pH is 11.17 and salinity is 170 ppt. At room temperature & 71:55hr, the oil recovery are (6.89%, 5.80%, 5.33%), respectively. The cumulative oil recovery is increases gradually with increase oven temperature from room temperature to (30, 40, 50, 60, and 70°C). At 70°C & 817:45hr, the cumulative oil recovery are (63.05%, 55.16%, 54.41%), respectively. Figure 14 shows the result of cores (S107& S104) with pH is 7 and salinity is 170 ppt, and also shows the results of (S316 & S311) with pH is 4 and salinity is 170 ppt. At 40°C & 286:00hr, the oil recovery is (1.89%, 4.00%) and (0.12%, 2.28%), respectively. At
70°C & 1201:00hr, the cumulative oil recovery reach with the maximum rate to (21.76%, 19.20%) and (24.01%, 21.29%), respectively. Figure 14 shows sandstone core that aged in oil for long time period with change salinity to 23 ppt (S307, S303) and 10 ppt (S116, S114) with constant pH is 11.17. At 216:30hr & 30°C, the cumulative oil recovery of (S116, S114) are (2.85%, 8.54%), respectively. At 169:30hr & room the temperature, the cumulative oil recovery of (S307, S303) are (8.97%, 9.49%), respectively. The cumulative oil recovery continues is increased from 30°C to 70°C to (31.37%, 30.50%) for (S116, S114) and (70.01%, 56.95%) for (S307, S303), respectively.

4.2.3 **Comparison the effects between oil recoveries (carbonate rocks).** Figure 15 shows the comparison between oil recoveries with different carbonate cores, temperature, aging time, pH, and salinity. The cumulative oil recovery is approximate and reasonable between 51% and 53.94% in cores (C211, C212, and C213) with pH is 11.7 and 170 ppt. While pH=7 and pH=4 is different, the cumulative oil recovery in core (C210, C214) with pH is 7 is higher than with pH is 4 (C413). The cumulative oil recovery in cores (C407, C409) with low salinity is higher than that with high salinity.

4.2.4 **Comparison the effects between oil recoveries (sandstone rocks).** Figure 16 shows the cumulative oil recovery in cores (S105, S115, and S102) with high pH and salinity. The cumulative oil in (S107, S104) with pH is 7 is lower than in (S316, S311) with pH is 4. In core (S303, S307) with high salinity (23 ppt) the cumulative oil recovery is higher than with low salinity for core (S114, S116).

4.2.5 **Results of Carbonate core samples that aged in oil for Short time period.** Figure 17 shows the oil recovery on carbonate core (C009) with short time, high pH, and salinity. At 46:30hr & room temperature, the oil recovery is (12.11%) and at 50°C & 622:00hr it is 15.14%. After that the cumulative oil recovery increases to 18.16%. At 886:30hr & 70°C, the cumulative oil recovery increase to 60.56%.
Figure 18 shows the effect of pH is 7 and pH is 4 with constant salinity is 170 ppt on oil recovery. At 160:30hr, the cumulative oil recovery reach to (38.90%, 23.05%) in cores (C002, C006) with pH is 7. While are (3.91%, 26.53%) in (C001, C003) with pH is 4 at 30°C. At 40°C & 309.30hr, the cumulative oil recovery continues increasing in (C002) is (48.24%), and at (51.87%) in (C006) at 500:30hr. At 454:00hr, the cumulative oil recovery reach to (5.86%) in (C001), where it reach to (36.09%), while in core (C003) at 405:30 hours. At 1123:00hr & 70°C, the cumulative oil recovery increase gradually and reached (57.57%, 72.04%) in (C002, C006), and to (39.11%, 48.83%) in core (C001, C003), respectively. Figure 19 shows cores (C004 & C005) with 10 ppt and cores (C008 & C007) with 7 ppt at constant pH is 11.17. At 118:30hr & room temperature, the cumulative oil recovery is (48.06%, 50.97%) in (C004, C005). At 260:30hr, the cumulative oil recovery is (23.77%, 20.56%) in (C008, C007). At 40°C &333:30hr, the cumulative oil recovery increase is (40.56%) in (C008). At 454:00hr, the cumulative oil recovery is (41.12%) in core (C007). At 357:00hr, the cumulative oil recovery is (57.67%) in core (C004), while is it still stable in core (C005). The cumulative oil recovery increase exponentially with increasing the aging time 1123:00hr & 70°C to (53.15%, 56.55%, 58.87%, 54.37%) in (C008, C007, C004, C005), respectively.

Figure 20 shows cores (S009 & S010) with pH is 11 and salinity is 170 ppt for short time. At 118:00hr & room temperature, the cumulative oil recovery is (41.19%, 7.87%) in cores (S009 & S010), respectively. At 40°C & 263:00hr, the cumulative oil recovery increase gradually until reach for core (S009) is (72.31%), and at 360:00hr in (S010) is (28.33%). The cumulative oil recovery is increasing with increasing the temperature to 70°C for (S009, S010) to (81.47%, 64.53%) at 981:00hr, respectively.
cumulative oil recovery increase exponentially are (18.58%, 54.40%, 49.60%, 15.88%) in (S006, S004, S001, S002), respectively. Figure 22 shows (S008, S007) with 23 ppt and for (S003, S005) with 10 ppt and constant pH is 11.17 with short time. At:30hr & with room temperature, the cumulative oil recovery for (S008, S007, S003, S005) are (14.12%, 16.51%, 71.46%, 7.46%), respectively. At 1123hr & 70°C, the cumulative oil recovery for (S008, S007, S003, S005) are (72.97%, 72.86%, 73.3%, 43.52%), respectively.

Figure 17. Effect of GWLI on cumulative oil recovery for carbonate that aged in oil for short time.

Figure 18. Effect of pH on cumulative oil recovery for carbonate that aged in oil for short time.

Figure 19. Effect of salinity on cumulative oil recovery for carbonate core that aged in oil for short time.

Figure 20. Effect of GWLI on cumulative oil recovery for sandstone that aged in oil for short time.

4.2.6 Comparison the effects between oil recoveries (carbonate rock). Figure 23 shows carbonate rocks with salinity (23 ppt, 10 ppt) and acidity (pH=7 & pH=4). The cumulative oil recovery with salinity 23 ppt and 10 ppt are approximate and reasonable between 53.15% and 58.87% for (C008, C007, C004, and C005). The cumulative oil recovery in (C006) with pH=7 is very high compared to (C001, and C003), and they are (57.57%, 72.04%, 39.11%, 48.83%) in cores (C002, C006, C001, C003) respectively. The cumulative oil recovery for core with salinity 10 ppt is higher than 23ppt, they are (58.87%, 54.37%) in (C004, C005), respectively, and to (53.15%, 56.55%) in (C008, C007), respectively.

4.2.7 Comparison the effects between oil recoveries (sandstone rocks). Figure 24 shows cores (S008, S007, S003) with salinity 23 ppt and 10 ppt and the oil recoveries are very high. In core (S006, S004) and (S001, S002) with pH=7 and pH=4, respectively. The oil recovery was very small reach maximum to 45.40% in core sample S006. In cores (S004, S001, and S002) are (18.58%, 4.10%, 15.88%). In core (S009, S010) with high salinity and high pH, the cumulative oil recovery is high reach to maximum recovery.
Conclusion and Recommendation of the Study
SIT was conducted by GWLI with pH is 7 & 4 and salinity is 23 ppt & 10 ppt for long and short aging time. GWLI acidity (pH) has impact effect on oil recovery, when the pH is 4 the oil recovery is higher than pH is 7. The oil recovery without change the salinity and the acidity of GWLI is higher. The oil recovery is increased with decreased the salinity of GWLI. The oil recovery in sandstone with original properties of GWLI is higher than with change any properties. The aging time has impact effect on oil recovery, it decreased with increasing aging time and increasing with decreased aging time. Hopefully, the research findings shown in this study can possibly be useful for references and for operating companies as an important source for understanding and visualizing the effects of pH, salinity and aging core in oil, on oil recovery from sandstone and carbonate reservoirs using GWLI. SIT shuld have amott cell that provides more accurate results. If the amott cell is not available, then SIT must has wider diameter pipe, in order to let the oil freely from the core samples. The amott cell shuld be in one place and do not move it, only in emergency case.

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