Article

EFFECTS OF ALKALINE/POLYMER/NANOFLUIDS ON OIL RECOVERY AT HARSH RESERVOIR CONDITIONS

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Abstract

This work investigates the modeling and optimization of different flooding scenarios using three types of alkaline/xanthan gum/and SiO₂ nanopowder at severe reservoir conditions of high temperature and high salinity. The rheological properties of the displacing fluids in addition to physical properties of the crude oil were investigated at simulated reservoir environment. Flooding runs conducted on linear sand pack assembly using different concentrations of the flooded slug. Moreover, the wettability alteration assessed at different slug concentrations. The results indicate that the higher oil recovery was achieved at 1.0 wt. % NaOH, 1000 ppm of xanthan gum and 0.05 wt. % SiO₂.

Keywords: Xanthan gum; Oil recovery; Displacement flooding; and Nanofluids.

1. Introduction

Alkaline flooding can lead to several improvements to increase oil recovery. First, the wettability alteration from oil- wet to water-wet by changing the pH of the solution ^[1]. Secondly, Alkalis can react with acids that exist in oil- producing in situ surfactant which can significantly decrease the interfacial tension ^[2]. High temperature can lead to better alkaline flooding efficiency. This decreases the contact angle thus, decreases the adhesion tension which will decrease the IFT ^[3]. However, if alkaline flooding was applied in limestone reservoirs, the interactions of injected fluids can lead to permanent and severe reductions in permeability. Polymer flooding is commonly known as the chemical solution that improves the mobility ratio and sweeping efficiency by increasing the viscosity of water, forming a piston-like a displacement which increases the oil recovery ^[4]. Two main polymers are used in enhancing the oil recovery, which is hydrolyzed polyacrylamide (HPAM) and xanthan gum (XG) ^[5]. Polymer viscosity increases by increasing the concentration or molecular weight. By polymer flooding, the sweep efficiency and microscopic oil displacement efficiency become favorable ^[6-7]. However, the polymer may lead to chemical adsorption and retention which may decrease the permeability and lead to formation damage near the well ^[8-9].

Temperature can negatively affect the efficiency of the solution. It decreases the polymer viscosity by chemical reactions that crack the bonds between the molecules of polymer. Thermal degradation occurs if the polymer is kept at a high temperature for a long time. If the solution viscosity decreases, precipitation occurs increasing the adsorption which decreases the oil recovery ^[10]. In the last two decades, nanoparticles have been taking the highest interest in EOR. Nanoparticles can migrate for a longer distance than any colloidal solids, it can withstand high-temperature reservoir conditions, and also nanoparticles can cover 100 times more surface area than micron particles which will increase the chance of interaction between the particles and the oil zone ^[11-12]. Silica dioxide is the type of nanoparticles which

can decrease the interfacial tension and alter the wettability to more water-wet [13-14]. The combination of chemicals also played an obvious role in increasing the oil recovery, when alkaline is added to the polymer solution, the consumption of alkaline becomes lower than when used in alkaline flooding alone ^[15]. Sodium hydroxide is considered the optimum alkali type to be combined with polymers either xanthan gum or HPAM, it lowered the IFT more than any other type of alkalis used ^[5]. However, it was concluded that alkali has two basic effects on polymer mobility, it increases the salt effect and it also increases the hydrolysis effect. Hydrolysis effect increases the viscosity while the salt effect decreases it. The balance between the two effects can obtain certain results. Generally, the salt effect is always greater which concludes that polymer viscosity becomes lower when alkaline concentration is added ^[16]. Alkaline polymer flooding can lead to polymer adsorption reduction. Also, polymer brings alkaline to the front of the flooding and makes it in contact with the oil to reduce the IFT. Polymer and alkaline form an efficient system, in which alkaline improves the sweep efficiency done by polymer, and polymer improves the IFT reduction when bringing alkaline in contact with oil zone ^[17]. Mansour et al. 1997 ^[18] studied the effect of alkalis on the PH and water viscosity. Their results showed that the highest oil recovery percentage was obtained at 1 wt. % NaOH and 1.5 wt. % of KOH concentrations. The highest percentage of recovery was then obtained when 1000 ppm bio-polymer was added. The crude oil used in this experiment has a high acidity number equal to 14.8 mg KOH/g. This high acidity number will allow reactions to occur between alkalis and organic acids which exist in the crude oil ^[19]. These chemical reactions will form surfactants, foams, and emulsifications which can significantly decrease the IFT. This phenomenon will reduce the capillary pressure between the oleic and aqueous phase, and break the molecules of large particles which are trapped into smaller ones due to the reduced water-oil IFT ^[20].

2. Experimental work

One type of each polymer and nano-particles was used, namely, xanthan gum and silicon dioxide respectively. Three types of alkalis are used namely, [sodium hydroxide, potassium hydroxide, sodium carbonate]. The porous medium used in this study is unconsolidated sandpack. The sand size used was 300 μ m. The diagram of the displacement apparatus used in this study is shown in Figure 1.



Figure 1. Displacement set up

It consists of a sandpack with an inside diameter of 8.3 cm and length 33.2 cm. Filters and screens are installed at both ends of the apparatus to decrease the endpoint effects and to obtain a good distribution of fluid flow through a porous medium. Two pressure valves were installed at the inlet and outlet of the model to measure the pressure drop. Three tanks are used to inject fluids into the sandpack model: Crude oil, formation water and chemicals mixture solutions. An electrical coil is made to increase the temperature of the sandpack and its

fluids contained. The temperature is stabilized at 71.1°C. The thermometer is used to measure the temperature across the sandpack. At 71.1°C, the sandpack model is saturated with 15 wt. % brine solution and crude oil was then injected to displace the brine water to irreducible water saturation. Two displacement mechanisms are applied after the initiation. The first mechanism is by injecting the mixture in a tertiary recovery stage, using water flooding followed by chemical flooding. The second mechanism is by injecting the mixture of chemicals directly without using waterflooding in the secondary recovery stage. The pressure, production rates and oil recovery were recorded at 71.1°C & 15 wt. % NaCl. Chemicals were prepared just before the injection to avoid any effect of precipitation or exposure to air ^[21-24].

3. Results and discussion

3.1. Chemicals rheology

The rheology was studied for xanthan gum [1000 ppm] concentration at shear rates [10, 30, 100, 300, 600] RPM. First, the effect of temperature was shown by three different temperature degrees [25°C, 50°C, 70°C]. Secondly, the effect of salinity on rheology was shown at four different weights [3.5%, 5%, 10%, 15%]. The effect of adding alkalis and nano- silica particles on xanthan gum was studied at 3.5 wt% salinity and room temperature 25°C ^[25-26].

3.1.1. Effect of temperature on rheology of xanthan gum

Temperature can play an obvious role in affecting the viscosity of xanthan gum. Increasing temperature can lead to a high reduction in viscosity as shown in Figure 2. The viscosity at 1000 ppm concentration of bio-polymer was 52.4 cP. By increasing the temperature from 25° C to 50° C, viscosity was reduced to 38 cP, while when the temperature was increased to 70° C, viscosity reached 30.7cP. The reduction was noticed to be about 40% of xanthan gum initial viscosity. However, the reduction from 25° C to 50° C was observed to be larger than the reduction of viscosity from 50° C to 70° C.

3.1.2. Effect of salinity on rheology of xanthan gum

Figure 3 shows the effect of different salinity weights on 1000 ppm concentration of xanthan gum. At room temperature and low salinity [3.5 wt. %], viscosity was found to be 52.4 cP. By increasing salinity by a certain weight, viscosity was reduced to 46.9 cP, 41.3 cP, and 36.7 cP for 5 wt. %, 10 wt. % and 15 wt. % respectively. At low shear rates, the viscosity of xanthan gum was considerably affected by salinity, when increasing salinity from 3.5 wt. % to 15 wt. % the reduction of viscosity was about 30 %. The range of reduction while increasing salinity was almost equal for all the four weights used.





Figure 2. Effect of temperature on xanthan gum at 3.5 wt. % salinity

Figure 3. Effect of salinity on xanthan gum at room temperature

3.1.3. Effect of alkaline addition on rheology of xanthan gum

Sodium hydroxide, sodium carbonate, and potassium hydroxide were added to the polymer at two concentrations (1 wt. % and 1.5 wt. %). For NaOH, the major effect which affected the

viscosity was the salt effect, as shown in Figure 4. When 1 wt. % and 1.5 wt. % NaOH were added to xanthan gum, the viscosity was reduced from 46.9 cP to 41.3 cP and 40.1 cP respectively. KOH addition was also affected by the salt effect but not so much as sodium as depicted in Figure 5. The viscosity slightly decreased when 1 wt. % KOH was added, and at 1.5 wt. % viscosity was reduced from 46.9 cP to 43.1 cP. This proves that KOH has an equilibrium between the salt effect and hydrolysis effect when a low concentration of potassium hydroxide is added. On the other hand, when sodium carbonate was added at 1 wt. % concentration, the viscosity increased due to hydrolysis effect from 46.9 cP to 48.3 cP, however when 1.5 wt. % was added the salt decreased the viscosity to 43.6 cP as shown in Figure 6.













3.1.4. Effect of adding SiO₂ nanoparticles on rheology of XG/alkali solution

As shown in Figures 7-9, adding SiO_2 to xanthan gum/alkalis solutions increases the viscosity of the chemicals mixture. Two concentrations of nanoparticles were used (0.05 wt. % and 0.1 wt. %).



Figure 7. Effect of adding SiO₂ on XG-NaOH solution



Figure 8. Effect of adding SiO2 on XG-KOH solution



Figure 9. Effect of adding SiO₂ on XG- Na₂CO₃ solution

3.2. Effect of alkali mixtures on secondary oil recovery

Figure 10 shows the effect of KOH with different combinations on the oil recovery factor. Firstly, KOH was used alone to displace the oil. Secondly, xanthan gum polymer with a concentration of 1000 was added to KOH. Finally, SiO_2 at a concentration of 0.05 and 0.2 wt. %

was added to KOH. The highest cumulative recovery obtained was by combining 1.5 wt. % KOH/ 1000 ppm XG and 0.05 wt. % SiO₂. In the waterflooding base run, the oil recovery factor was found to be 44 % of the original oil in place. By adding 1.5 wt. % KOH, the oil recovery factor was increased by 10 %. By using XG polymer the recovery factor reached 71 % which means that adding polymer increased recovery by 17 %. By adding 0.05 wt. % of nano silica, the oil recovery factor was increased by 2 %. However, the high concentration of 0.2 wt. % of silica nanoparticles (SiO₂) did not increase the oil recovery and this may be due to nanoparticle adsorption. The next four runs investigate the effect of Na₂CO₃ secondary oil recovery factor by 13 % more than the water flooding scenario as shown in Figure 11.







Figure 11. Effect of sodium carbonate on oil recovery

By adding polymer to Na₂CO₃, the recovery factor was increased by 10 % to reach 67 % of the original oil in place. Silica nanoparticles with Na₂CO₃ had a positive impact on Recovery. Increasing the concentration of silica nanoparticles increased recovery. At 0.05 wt. % silica nanoparticles, the oil recovery factor was increased to 74% while at 0.2 wt. % of silica nanoparticles, the oil recovery factor was increased to 76 %. The last four experimental runs for secondary recovery stage were made for sodium hydroxide combinations as shown in Figure 12. NaOH flooding alone has increased the recovery factor by 17% more than the base water flooding case. NaOH was also more efficient than any other alkaline. When XG was added, the recovery factor was increased by 19% to reach 80% of the original oil in place. By adding

silica nanoparticles with a concentration of 0.05 wt. % to NaOH, the recovery factor was found to be 82% of the original oil in place. However, increasing the concentration of silica nanoparticles gives similar results to KOH; adsorption played a role in reducing the oil recovery ^[27].



Figure 12. Effect of sodium hydroxide oil recovery

3.2.1. Comparison between alkali mixtures effects on secondary oil recovery

Figure 13 depicts the effect of NaOH, Na₂CO₃, and KOH on the secondary oil recovery factor compared to the effect of water flooding alone. By using waterflood, the oil recovery factor was found to be 44 % of the original oil in place. The oil recovery factors were found to be 61 %, 57 and 54 % of the original oil in place by using NaOH, Na₂CO₃, and KOH respectively. The highest recovery factor of 61 % is due to the high efficiency of NaOH in lowering the interfacial tension and its high pH value.



Figure 13. Effect of different alkalis on SOR

Adding polymer xanthan gum to alkalis as a secondary recovery has increased the oil recovery factor by a range of 10 to 20 % of the original oil in place as shown in Figure 14. The highest oil recovery factor was found to be 80 % of the original oil in place by using NaOH/XG. KOH/XG gives oil recovery factor of 71% and Na₂CO₃/XG gives a recovery factor of 67 % of the original oil in place. Silica nanoparticle with a low concentration of 0.05 wt. % was combined with alkalis and XG. The oil recovery factors were found to be 82, 74 and 71 % of the original oil in place by adding silica nanoparticle at low concentration to NaOH/XG, KOH/XG, and Na₂CO₃/XG respectively as presented in Figure 15.







Figure 15. Effect of polymer XG with alkalis on SOR



Figure 16. Effect of alkalis/XG/silica 0.05 wt. %. on SOR

Adding silica nanoparticles has increased the oil recovery factor by 2 % of the original oil in place. Silica nanoparticle with a high concentration of 0.2 wt. % was combined with alkalis and XG. The oil recovery factors were found to be 79, 78 and 76 % of the original oil in place by adding silica nanoparticle at high concentration to NaOH/XG, Na₂CO₃/XG, and KOH/XG respectively as shown in Figure 16. Adding silica nanoparticles at high has increased the oil

recovery factor by 7 % of the original oil in place with Na_2CO_3/XG and decreased the recovery factor with NaOH/XG and KOH/XG^[28].

3.3. Effect of chemicals on tertiary oil recovery at harsh conditions

The same procedures were made for tertiary recovery stage. Finally, a comparison between secondary and tertiary recovery stages is made to investigate the optimum recovery with the optimum technique.

3.3.1. Effect of alkali mixtures on oil recovery by tertiary recovery stage

The same procedures were made for tertiary technique; the difference is displacing initially the oil by brine with 3.5 wt. % salinity. After recording the recovery obtained from the secondary water flooding technique, the tertiary technique has proceeded. As shown in Figures 17-19, all water flooding processes gave approximately the same results, giving 43-44% cumulative recovery. From 400 cc of PV to 600 cc of PV injected, the increase rate was not very efficient. Thus, it's preferable to start the tertiary recovery stage at 400 cc PV, which is equal to 0.67 PV. Comparing the different combinations, results concluded that the most efficient mixture for potassium was 1.5 wt. % KOH/1000 ppm xanthan gum and 0.05 wt. % SiO₂, similar to the secondary stage but with less recovery reaching 70%. In this process, the recovery obtained by the combination of polymer with KOH was higher than when adding 0.2 wt. % Silica. This assures that the high concentration of Nano can produce a negative impact on recovery by increasing the adsorption. Similar to the analysis obtained for KOH, it is preferable to start tertiary technique at pore volume close to 400 cc PV or 0.67 PV, also, recovery obtained by secondary stage was more efficient than tertiary. As shown in Figure 19, the highest value of recovery obtained in tertiary technique was equal to 73% which is still less than 76% obtained by secondary. The mixture with the highest recovery was 1.5 wt. % Na₂CO₃/ 1000 ppm XG and 0.2 wt. % SiO₂. Using high concentration nano with sodium carbonate was more efficient by 6% recovery from using low concentration with sodium carbonate. According to secondary and tertiary stages investigating sodium carbonate, it is clear that the combination of SiO₂ and Na₂CO₃ is more efficient than being combined with KOH or NaOH $^{[4]}$.



Figure 17. Sodium carbonate tertiary recovery versus pore volume

The final four runs describing the effect of combining NaOH with XG and SiO₂ when proceeding in the tertiary recovery stage was shown in Figure 20. Adding NaOH after water flooding increased the recovery by 8%, this value was considered low compared with 17% which was recovered from the secondary technique. However, adding XG increased the recovery similar to when it was used as secondary. This phenomenon means that the polymer was not affected by the technique while NaOH was. Adding low and then the high concentration of SiO₂

increased slightly the recovery until it reached 73%, still less than 82% obtained when the mixture was used in the secondary recovery stage.







Figure 19. Potassium hydroxide tertiary recovery versus pore volume

3.3.2. Comparison between alkali mixtures increasing oil recovery by tertiary recovery stage

First, as a tertiary displacement recovery stage, all alkalis had close displacement efficiencies ranging from 0.49 to 0.53% which is the highest obtained by Na₂CO₃ as shown in Figure 20. Second, tertiary technique did not differ much in recovery percentage when the polymer was added, the polymer was not affected by changing the technique as alkaline. The highest recovery for this alkali/XG combination was NaOH/XG which gave a recovery of 70% as shown in Figure 21. Third, for tertiary recovery stage when low concentration (0.05 wt% SiO₂) was added as shown in Figure 22, the low concentration of SiO₂ increased slightly the recovery of the three alkalis, having the highest recovery difference equal to 4% for KOH. It only increased by 1% for NaOH which is still having the highest displacement efficiency value. And finally, NaOH mixture with high SiO₂ concentration was not reduced as shown in Figure 23, recovery for NaOH increased by 2%. While Na₂CO₃ increased by 6%, this increase of recovery done by Na₂CO₃ mixture allowed it to have the same recovery as NaOH having both a recovery of 73%. However, Recovery obtained by KOH mixture with high SiO₂ concentration was not reduced as not more efficient than the low concentration of nano SiO₂.

















3.4. Comparison between oil recovery by secondary stage and tertiary stage

As shown in Table 1, all secondary recovery stage runs had higher recovery than the tertiary recovery stage runs. The highest difference was for low concentration of NaOH/XG equal to 11% recovery. Before the secondary stage, the residual oil in the sandpack or in the reservoir will remain at its maximum volume, which means the quantity of acids in situ is considered larger, this will aid alkalis to react with acids producing surfactants and foams reducing the interfacial tension. However, in the tertiary stage, water flooding will be already applied to produce a percentage of oil, in our case, it's 44%. This will affect the acidity number and reduce the number of reactions that will happen. The interfacial tension will not be reduced as similar to the secondary stage.

Chemical solutions	Recovery %			
	Secondary	Tertiary		
WF	44			
NaOH	61	52		
NaOH/XG	80	70		
NaOH/XG/LCS	82	71		
NaOH/XG/HCS	77	73		
КОН	54	49		
KOH/XG	71	66		
KOH/XG/LCS	74	70		
KOH/XG/HCS	73	64		
Na2CO3	57	53		
Na2CO3/XG	67	65		
Na2CO3/XG/LCS	71	67		
Na2CO3/XG/HCS	76	73		

Table 1. Comparison between secondary and tertiary recovery stages

3.5. Effect of chemicals on rock wettability

The effect of chemicals on wettability alteration was evaluated as indicated in Figures 24-35.









Figure 26. NaOH relative permeability curve









Figure 28. NaOH/XG/ SiO₂ LCS relative permeability curve



Figure 30. KOH/XG/LCS relative permeability curve



Figure 32. Na₂CO₃ Relative permeability curve





Figure 29. KOH relative permeability curve



Figure 31. KOH/XG/HCS relative permeability curve



Figure 33. Na₂CO₃/XG relative permeability curve



Figure 34. Na₂CO₃/XG/LCS Relative permeability curve

Figure 35. Na₂CO₃/XG/HCS relative permeability curve

As shown in Table 2, initially the sandpack model was considered a water wet tank having the intersection of water relative permeability and oil relative permeability at a saturation equal to 0.54, such if the intersection is at a saturation larger than 0.5, It means the rock is water wet. In another meaning, when the intersection of relative permeabilities is on the right, occurring at a saturation more than 50% means that the rock is more saturated by water than oil and it will be considered water wet. The more the intersection is shifted right, the more the residual oil decreases and the rock will be more saturated by water [more water wet]. As shown in Table 2, when the polymer was added to all Alkalis, it didn't have any considerable effect on wettability, its role in this experiment was to improve the sweeping efficiency and mobility ratio, but not the wettability. On the other hand, all three alkalis and silica particles had an obvious effect on Relative permeability and wettability alteration.

First, sodium hydroxide shifted the intersection rightly by a different saturation of 9%. Also, by increasing the silicon dioxide's concentration, the wettability was altered to a more water-

wet rock by 5% for LCS and 6% for HCS. sodium hydroxide and silicon had a positive influence on wettability altering it to be more water wet, this improved the displacement of oil and increased the recovery. Secondly, sodium carbonate had a negative influence on the wettability, it shifted the intersection of relative ratios left, which altered the wettability to less water wet, it shifted it from saturation equal to 0.54 to 0.52. However, by increasing nanoparticles on solution shifted the intersection right again, the intersection reached a saturation of 0.63. Thirdly, potassium hydroxide had the highest effect on wettability. It shifted the intersection by 10% to the right. By adding LCS and HCS the alteration reached its maximum to 0.76 which transformed the rock from normal water-wet to strong water wet. The combination of potassium with silicon dioxide had an obvious effect on wettability, the alteration was more effective than the alteration done by sodium hydroxide.

Chemicals	Concentrations		Sw at Kro=Krw	Intersection shift (Sw)	
Water flooding	-			0.54	-
NaOH	1 wt%			0.63	0.09 R
NaOH-XG	1 wt%	1000 ppm		0.64	0.1 R
NaOH-XG-SiO2	1 wt%	1000 ppm	0.05 wt %	0.68	0.14 R
NaOH-XG-SiO2	1 wt%	1000 Ppm	0.2 wt%	0.69	0.15 R
Na ₂ CO ₃	1.5 wt%			0.52	0.02 L
Na ₂ CO ₃ -XG	1.5 wt%	1000 ppm		0.53	0.01 L
Na2CO3-XG-SiO2	1.5 wt%	1000 ppm	0.05 wt %	0.54	0
Na2CO3-XG-SiO2	1.5 wt%	1000 ppm	0.2 wt %	0.63	0.09 R
КОН	1.5 wt%			0.64	0.1 R
KOH-XG	1.5 wt%	1000 ppm		0.65	0.11 R
KOH-XG-SiO2	1.5 wt%	1000 ppm	0.05 wt %	0.68	0.17 R
KOH-XG-SiO2	1.5 wt%	1000 ppm	0.2 wt %	0.76	0.22 R

Table 2. Wettability alteration

4. Conclusion

Based on the results obtained from experimental work, the following conclusions were obtained:

- 1. The viscosity of polymer increases with increasing concentration and decreases with increasing the temperature or salinity, however, xanthan gum can be used in Harsh conditions due to its ability to withstand harsh conditions
- 2. By increasing the concentration of Alkalis, the IFT decreases. Na₂CO₃ obtained the minimum IFT comparing with the two other alkalis used
- 3. Secondary recovery technique is considered more efficient than tertiary recovery technique in a range between 7 to 10% more.
- 4. When comparing the three alkali mixtures, the optimum concentration was obtained by the combination of 1 wt% NaOH, 1000 ppm Polymer and low concentration 0.05 wt% nano, having a recovery of 82%
- 5. The optimum PV at which tertiary must be initiated is equal to 0.67
- 6. Wettability alteration was observed for all the chemicals used. Polymer had no effect on relative permeability. However, NaOH and KOH played an obvious role in changing wettability. Also, with increasing SiO₂ concentration the wettability significantly becomes more water wet.
- 7. Na_2CO_3 had a negative influence on wettability, it altered it to be weakly water wet.

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