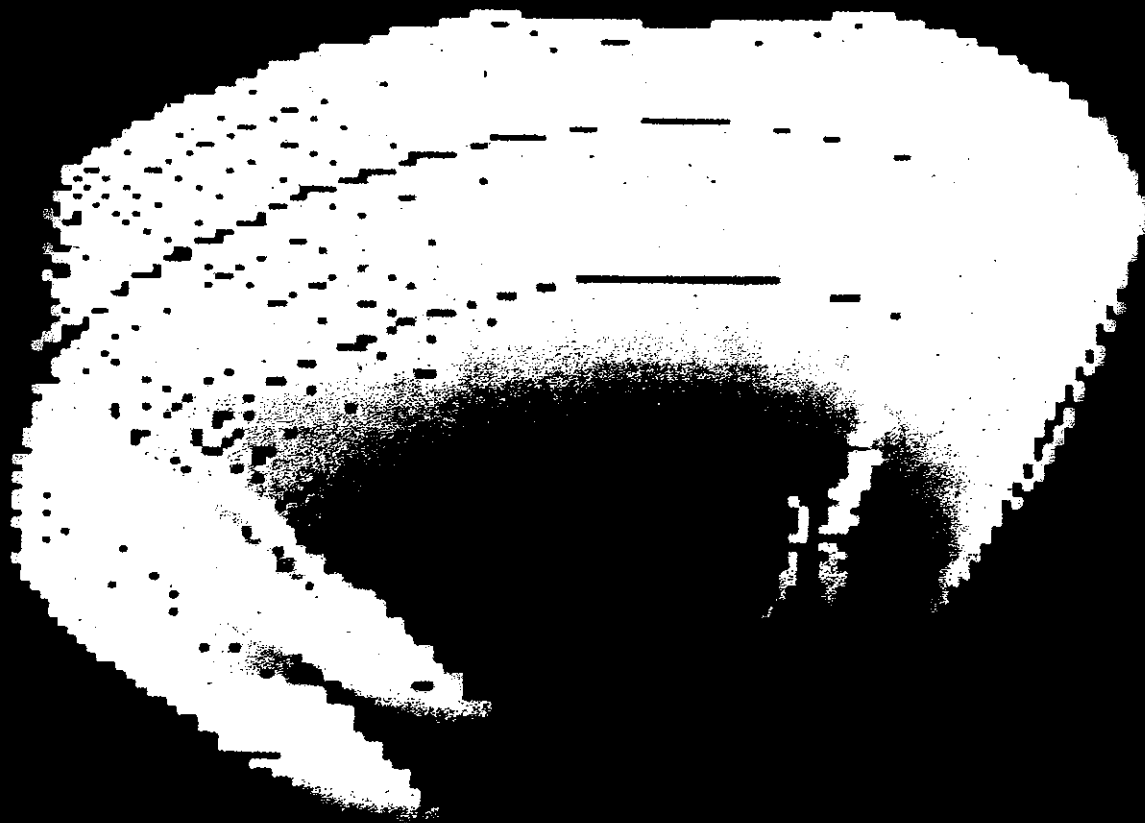


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Investigation of Polymer Adsorption on Rock Surface of High Saline Reservoirs

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Abstract

Blocking or reducing water production from oil wells is a serious problem in oil industry. Two types of polymers namely, polyacrylamide (PAA) and polysaccharides (xanthan) have been investigated for adsorption on rock surface. The viscosity of both polymer solutions were first evaluated at different salinities, shear rates and concentrations. Afterwards, the solutions were injected into core samples to examine the adsorption on rock surface by calculating the resistance factor as well as the residual resistance factor. Also, the effect of the injection rate of polymer solution has been studied.

The results show that xanthan solution is tolerant of high salinity (20%), while PAA-solution is very sensitive to salt. Both polymer solutions show a pseudoplastic flow as function of shear rate. Although, the core sample experiments show that both polymer solutions suffer a reduction in the adsorption rate with salinity increase, xanthan shows acceptable values even with a salinity up to 20 % and a temperature of 52 °C. Therefore, xanthan can be recommended to shut off water in high salinity and high temperature reservoirs. It is also found that the lower the injection rate the higher is the adsorption on rock surface.

1 Introduction

More than 50 % of the original oil in place remains in subsurface reservoir after primary and secondary recovery processes [1]. Physical and geological factors are responsible for the low recovery. The main physical reasons are the existence of interfacial tension forces between solids and liquid, liquid and liquid and the difference between rheological properties of oil and water that results in the entrapment of immobile residual oil saturation in the formation. The main geological factor is the heterogeneity of the reservoir, which leads to a faster sweep of oil from zones with high permeability, leaving behind oil in low permeability zones. Excessive production of water as a result of heterogeneities or fractures often causes channeling of water coning. This is a problem of central importance for field operators [1].

A significant part of the residual oil can be recovered with technically proved enhanced oil recovery techniques [2]. Although, most of the reservoirs in the Middle East are in the primary and secondary recovery stages, substantial efforts in different research centers in the Middle East have been made to increase the lifetime of the reservoir using polymer solution as an EOR [3,4]. These efforts are presently concentrated on the reservoirs that are suffering early breakthrough due to reservoir heterogeneity or due to natural fractures connected to a water source and resulting in high water production mainly due to high salinity of the water. In some Middle East wells (Saudi Arabia, Kuwait and Iran), due to this early breakthrough the water cut increased to a value up to 40%, which leads to shut down of these wells. Lifting, treatment and disposal of the produced water become expensive and is environmentally harmful [4].

Several scenarios have been suggested to minimize or to control the water production by selective zonal isolation of layers with high water production. Oil industry has presented two methods to control water breakthrough. The first one is the mechanical isolation of layers with high permeability; which is suitable for non-communicated layers or for layers with low vertical permeability. Moreover, this method is applicable to layers with satisfactory thickness to set the necessary packers for the zonal isolation. The second method is devoted to water control using water-soluble polymers. This method can be applied in stratified reservoirs with communicated as well as non-communicated layers. Therefore, this method is more favorable than a mechanical one. Moreover, water-soluble polymers have been tested and used in oil fields under different reservoir conditions [5-10].

The main reservoirs in Saudi Arabia and the Arabian Gulf States consist of up to 10 layers (e.g. Arab C and Arab D) with different petrophysical properties and low layer thickness (5-10ft) [11]. Therefore, a mechanical isolation is not applicable because the layers are thin [6]. Most reservoirs contain significant heterogeneities in the areal and particularly in the vertical sense. This leads to preferential water entry into the more permeable zones and to a more rapid sweep out of these zones. In the areas of the reservoir that are contacted by the flooding water, oil recovery may be very efficient. The problem is that much of the reservoir remains untouched.

A polymer injected into the flooded-out zone of such a reservoir may recover very little oil from that zone. The effect of the polymer can be very beneficial, however, because of the fluid diversion it produces. The polymer will build up flow resistance in the portions of the reservoir it penetrates through the permeability

reduction or by increasing the viscosity of the displacing water. This increased resistance to flow will divert subsequently injected water into unswept or poorly swept areas. In most flooding operations that are initiated at high WOR's, fluid diversion will be much more significant than fractional flow or mobility ratio effects. Maximum benefits will likely be achieved if the effect of the polymer can be sustained over a long time. This tends to place a premium reduction on permeability as opposed to straight viscosity improvement, because permeability reduction can be very long lasting [8-9].

The polymer flooding technique involves the addition of a thickening agent (polymer) to the injected water to increase its viscosity. Although ultimate residual oil saturation is essentially unaffected, the addition of a polymer yields two benefits; reducing the total volume of water required to reach the ultimate residual oil saturation and increasing sweep efficiency due to improved mobility ratio. The economic success of reported projects has varied considerably [3, 5, 9, 12-13]. Successful projects have yielded increased recoveries of 5-15%. Many unprofitable projects were the result of inadequate reservoir description prior startup.

Flow through porous media should also depend on the retention, adsorption, inaccessible pore volume and entrapment caused by the polymer [4, 7, 10,14]. Adsorption or retention of a chemical on the rock surface influences its concentration in the solution, and thus its effectiveness for the flood process. The adsorption is an important screening parameter for polymers. A certain rate of adsorption is even desired to obtain adequate values for the residual resistance factor. Adsorption mechanisms are divided into physical and chemical adsorption. Physical adsorption means a relatively weak bond between the surface (adsorbent) and the adsorbed species (adsorptive). The forces are Electrostatic (Van der Waals). In chemical

adsorption a chemical reaction between adsorbent and adsorptive takes place [3, 6, 7].

In the present work, polysaccharide (xanthan) and polyacrylamide (PAA) are used to investigate the adsorption of polymer molecules on the surface of different core samples. Also, the factors affecting the adsorption of polymer such as polymer concentration, salinity, temperature and injection rate have been studied. To evaluate the effect of these factors on the polymer adsorption as well as the suitability of the tested polymers for permeability modification, an extensive core flooding tests have been performed in sandstone under different conditions to simulate the reservoir conditions in some Middle East reservoirs.

2 Experimental Work

In the present work materials and equipment used included the following: polymers, brine, core samples, flooding apparatus and viscometer. Their properties and specifications are described below.

2.1 Polymer Solutions

Two different commercial available polymers, polysaccharide (xanthan) and Polyacrylamide (PAA) have been used throughout this study.. Xanthan is a product of bacterial fermentation with an average molecular weight of 5×10^6 Daltons. Polyacrylamide has an average molecular weight of 3×10^6 Daltons. The polymer solutions were prepared by mixing a certain weight of powdered polymer in freshwater using magnetic stirring. A biocide (Formaldehyde) at 1000 ppm was added to all solutions prepared to prevent a bacterial degradation of the polymer. Formaldehyde can be effective in preventing degradation due to oxygen and is

generally recommended for field use because the unit cost is low compared with other chemicals such as hydrosulfite, and the handling problems are minimal. It is also an effective biocide. It continues to protect polymer solutions when they are exposed to additional oxygen after mixing. The desired salt concentration of polymer solution was reached by adding salts to freshly mixed polymer solutions. The solution was filtered using 5 μm filters to remove the solids or microgel.

2.2 Brine Solution

Synthetic model brines were applied in all solutions using 83 % (w/w) sodium chloride (NaCl) and 17 % (w/w) calcium chloride (CaCl_2). Brine solutions were prepared in different salt concentrations starting with 2.5 % (w/w) up to 20 % (w/w).

2.3 Core Samples

Core samples were cut from an outcrop of sandstone rock. The mineralogical composition was determined using X-ray diffractometer. The samples consist of quartz (86.8 wt.%), feldspar (5.1 wt.%), clay (6.8 wt.%) and other minerals (1.3 wt.%), which reflects almost the mineral composition of some Middle East reservoirs (Sandstone Formations). The core samples were washed and dried in an oven at 120 $^{\circ}\text{C}$ for 24 h. The dimensions of the cores range between 9.3 and 10 cm in length, and between 4.9 and 5.1 cm in diameter. Afterwards, the petrophysical parameters of the core samples were determined. Table 1 shows the obtained values of pore volumes, porosity, and absolute permeability.

Table 1. Petrophysical data of used core samples.

Core No.	Bulk Volume [cc]	Permeability [mD]	Porosity [%]
1	191	214	24
2	199	348	26
3	165	724	17
4	143	514	28
5	129	1170	39
6	173	850	31
7	196	379	27
8	193	380	29
9	188	591	29
10	185	699	28
11	162	612	28
12	185	206	23
13	200	544	28
14	201	1304	29

2.4 Viscosity Measurements

Brookfield viscometer, model LVT with a spindle was used to perform viscosity measurements. This viscometer provides apparent viscosity in the range of shear rates from 0.36 to 73.42 s⁻¹.

2.5 Flooding Apparatus

Flooding apparatus has been set up to conduct the required experiments. The main components of the flooding apparatus are fluid storage vessels, displacement pumps, Hock cell (core holder), and fraction collector. The pressure drop across the core was measured using pressure transducers.

3 Experimental Procedures

The effect of the salinity on the polymer solution was investigated with different salt concentrations. After preparation of the solutions, the viscosity was measured over the range of shear rates from 0.36 to 73.42 s⁻¹ to investigate the effect of the brine on the polymer solutions at constant temperature of 25 ± 1°C. After determining the effect of salinity on the polymer solution the flooding experiments were carried out. The experimental displacement procedure was established as follows for each sample. The core sample was placed in the core holder with rubber sleeve around it. A confining pressure was applied with hand pump (hydraulic oil up to 1000 psi). The core sample was evacuated using vacuum pump and was saturated with water at the appropriate salinity. The pore volume was measured and porosity was calculated. The core permeability was then calculated at constant injection flow rate by recording the pressure drop between the inlet and outlet sides using Darcy's equation:

$$k = \frac{q^* \mu^* L}{A^* \Delta p} \quad (1)$$

The core samples were then flooded with polymer solutions of different concentrations. The injection rate for all runs was maintained constant at 60 cm³/h,

which is equivalent to a frontal velocity of about 2.5 ft/day. The polymer concentrations selected for the displacement runs are 800 ppm and 1200 ppm of xanthan-solutions and 1500 ppm, 2000 ppm and 3000 ppm of PAA-solutions in different salt concentrations. The system temperature was kept constant at $25 \pm 1^\circ\text{C}$. Polymer flooding was continued until full adsorption is achieved which is indicated by a constant pressure drop and constant viscosity of the effluent. Resistance factor, which describes the ratio of the mobility of water to the mobility of a polymer solution, was calculated using the following equation:

$$RF = \frac{\lambda_w}{\lambda_p} = \frac{\Delta P_p}{\Delta P_w} \quad (2)$$

The core sample was flooded with brine and Δp was measured (Viscosity of effluent was observed). The residual resistance factor, which describes the ratio of the mobility of water measured before the injection of the polymer solution to the mobility of water after polymer injection, was calculated using the following equation.

$$RRF = \frac{\lambda_{wb}}{\lambda_{pa}} = \frac{\Delta P_{wa}}{\Delta P_{wb}} \quad (3)$$

4 Results and Discussion

Beside the study of the effect of brine concentration on polymer solution viscosity, a total of 16 displacement runs have been performed; 8 runs with variable salinity of the xanthan solutions, 6 runs with variable salinity of polyacrylamide solutions and the remaining 2 runs have been performed using xanthan solution of 1200 ppm and 800 ppm at temperature of 52°C (125°F). The effect of the injection

flow rate has been also investigated. The results are discussed in the following sections.

4.1 Effect of Shear Rate and Salt Concentration on Polymer Solution Viscosity

Figures 1-9 show the results of the experiments conducted on polymer solution viscosity. Figs. 1-5 are plotted for xanthan solution while Figs. 6-9 are drawn for PAA solution. Fig. 1 shows the viscosity of xanthan solution at different concentrations, dissolved in fresh water, as a function of shear rate. It shows that the higher the concentration the higher the viscosity. Increasing the shear rate reduces the polymer solution viscosity. At shear rate higher than 40 s^{-1} , the effect of polymer concentration vanishes. This means that increasing the shear rate drastically reduces the effect of polymer concentration. Also, shear rate higher than 14.7 s^{-1} is not recommended.

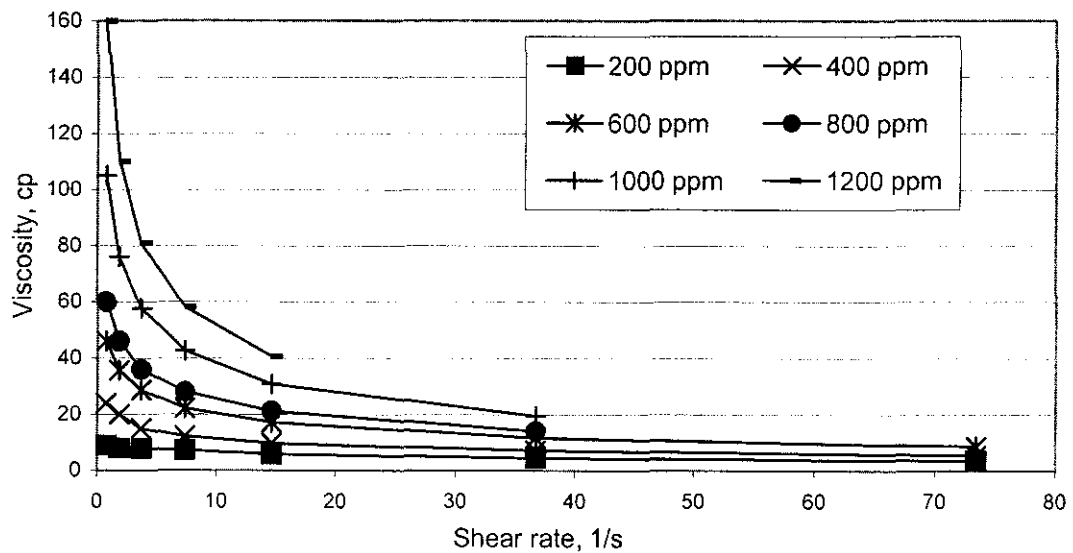


Figure 1. Viscosity of xanthan solution of different concentrations in fresh water

Figure 2 plots the viscosity of polymer solution dissolved in 10% brine as a function of the shear rate. The same trend can be observed for fresh water, but the viscosity

readings decrease. For example at 1200 ppm concentration and 14.7 s^{-1} , the viscosity is reduced from 40 cp in fresh water to 24 cp in 10% brine.

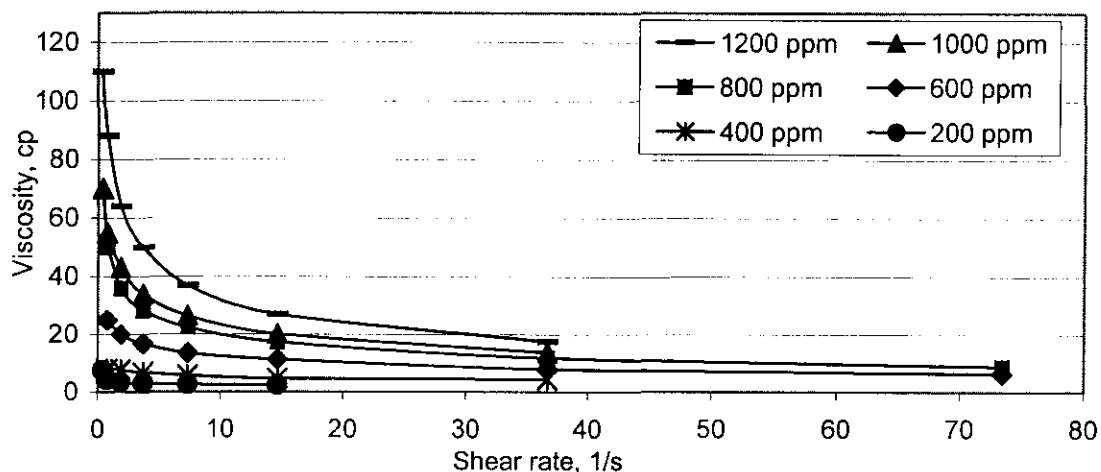


Figure 2. Viscosity of polymer solution of different xanthan concentrations in 10% brine

Figures 3 and 4 show the results at 15% brine and 20% brine. The same trend is observed for shear rate. Plotting the viscosity of polymer solution of 800 ppm and 1200 ppm concentration against brine concentration, Fig. 5, shows that the viscosity decreases by increasing brine concentration up to a certain value and then increases again. The minimum value depends on the concentration. The same results have been confirmed by *Ali et al.* [4].

Figures 6-9 show the results for PAA solutions. Fig. 6 shows the viscosity of PAA solution in 2.5% brine as function of the shear rate. It shows the same trend like xanthan but at higher concentration of PAA-polymer. PAA dissolved in fresh water is not included because the viscosity of the solution is out of the equipment range.

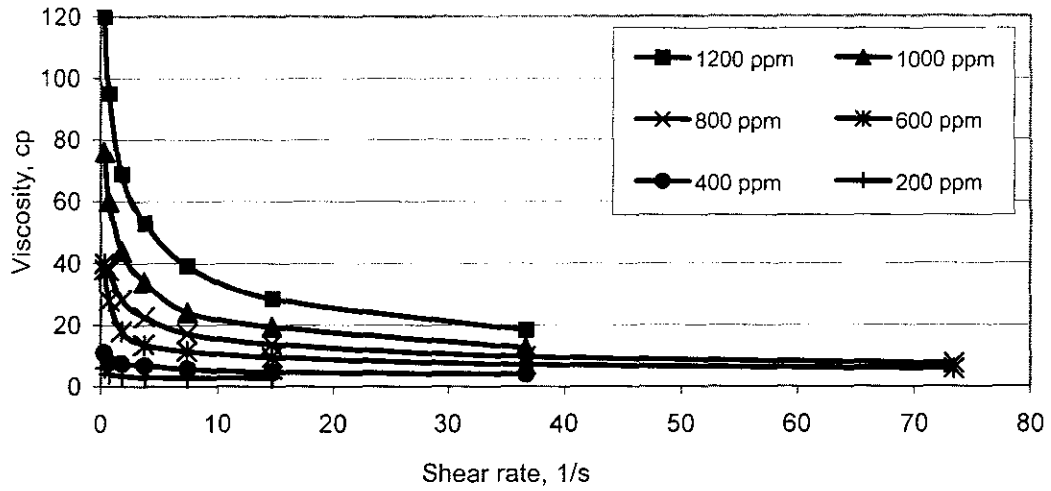


Figure 3. Viscosity of xanthan solution of different concentrations in 15% brine

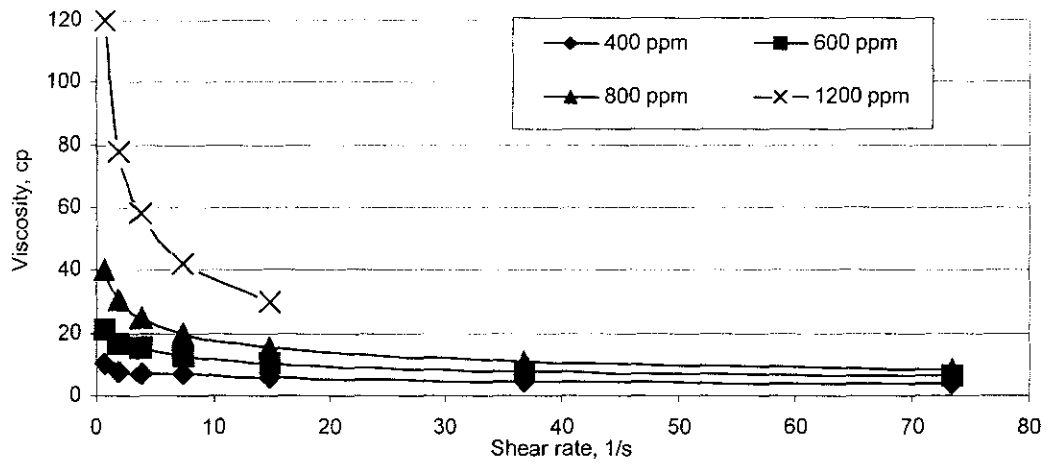


Figure 4. Viscosity of xanthan solution of different concentrations in 20% brine

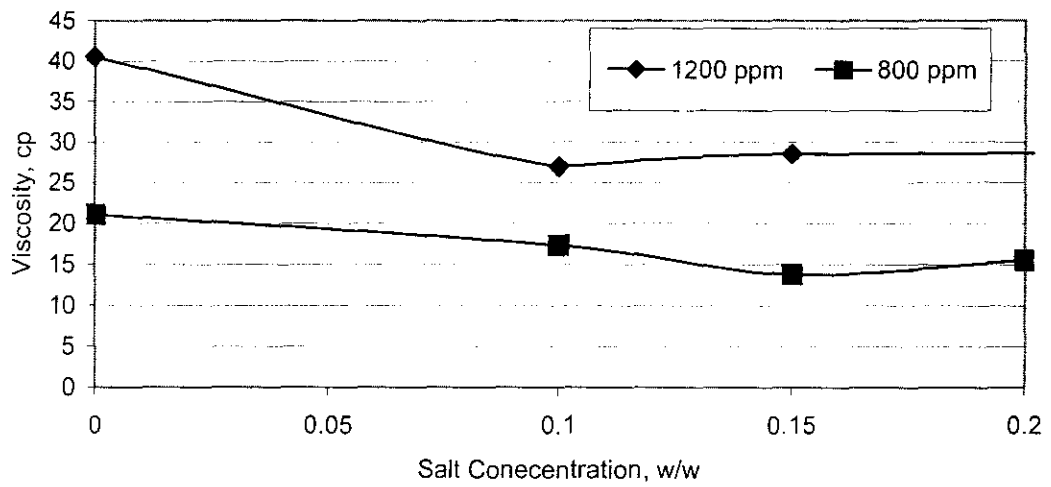


Figure 5. Effect of salt concentration on the viscosity of xanthan solution at constant shear rate (14.7 1/s)

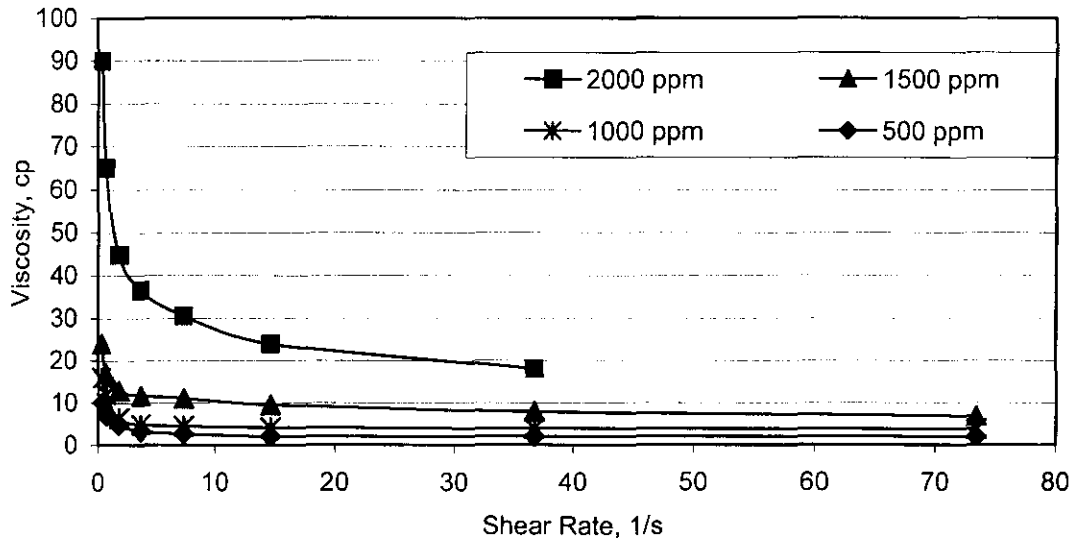


Figure 6. Viscosity of PAA solution of different concentrations in 2.5% brine

Figs. 7 and 8 plot the viscosity of PAA solution dissolved in 5% and 10% brine. Distilled water is a good solvent for both polymers. However, as salt is added, the electrolyte neutralizes the charge of polymer molecule and the force, which helped to extend the polymer molecule, decreases [5]. Thus, as salt concentrations are increased, the polymer molecule contracts and reduces the solution viscosity. To get a reasonable value of PAA polymer solution viscosity, polymer concentration has been increased greatly. This means that PAA is very sensitive to brine concentration. Plotting viscosity against brine concentration, Fig. 9, shows that the brine concentration reduces PAA solution viscosity drastically.

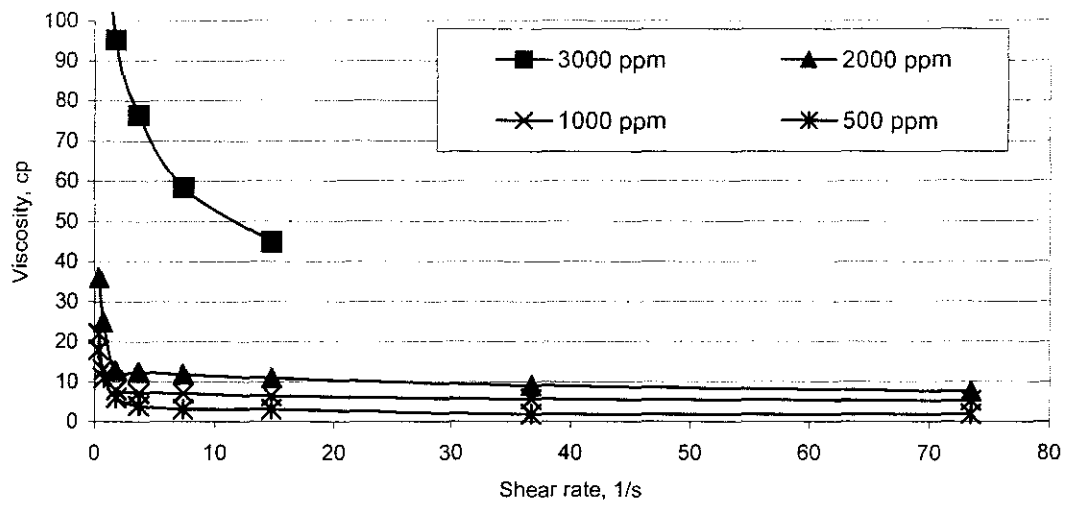


Figure 7. Viscosity of PAA solution of different concentrations in 5% brine

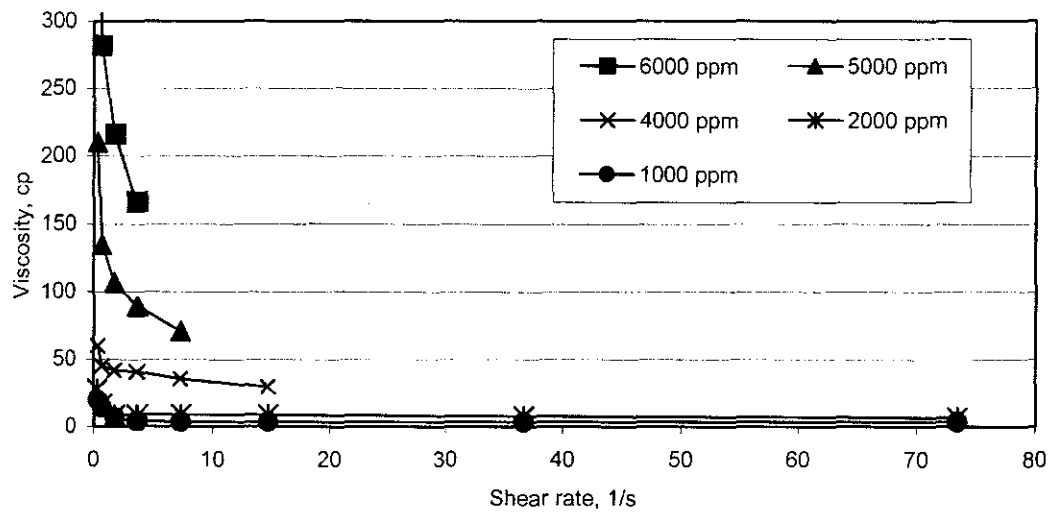


Figure 8. Viscosity of PAA solution of different concentrations in 10% brine

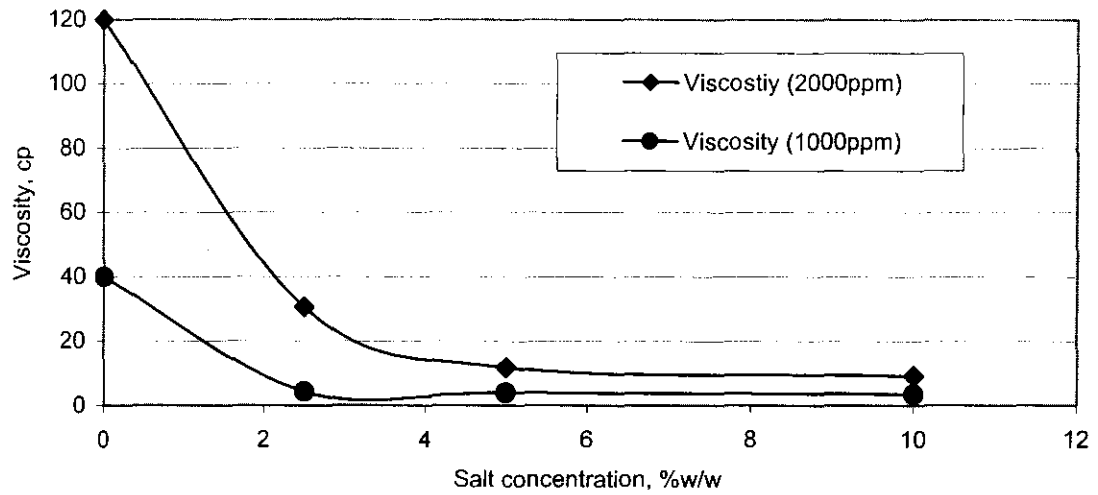


Figure 9. Effect of salt concentration on the viscosity of PAA at constant shear rate (14.7 1/s)

4.2 Polymer Adsorption on Rock Surface

To investigate the polymer adsorption on reservoir rock surface, resistance factor (RF) and residual resistance factor (RRF) are measured. Figs. 10 and 11 show examples of this measurement. Data are given in Tables 2 and 3. Table 2 shows the results of xanthan solution while Table 3 is for PAA solutions. An increase in the polymer concentration leads to higher value of RF and RRF for constant permeability. Increasing brine concentration reduces the RF and RRF. This is due to electrolyte that leads to the reduction in the extension of the polymer molecule. However, this reduction is not high in case of xanthan. This shows that xanthan yields high adsorption on the rock surface under high salinity, which means favorable properties for water control of the producing wells.

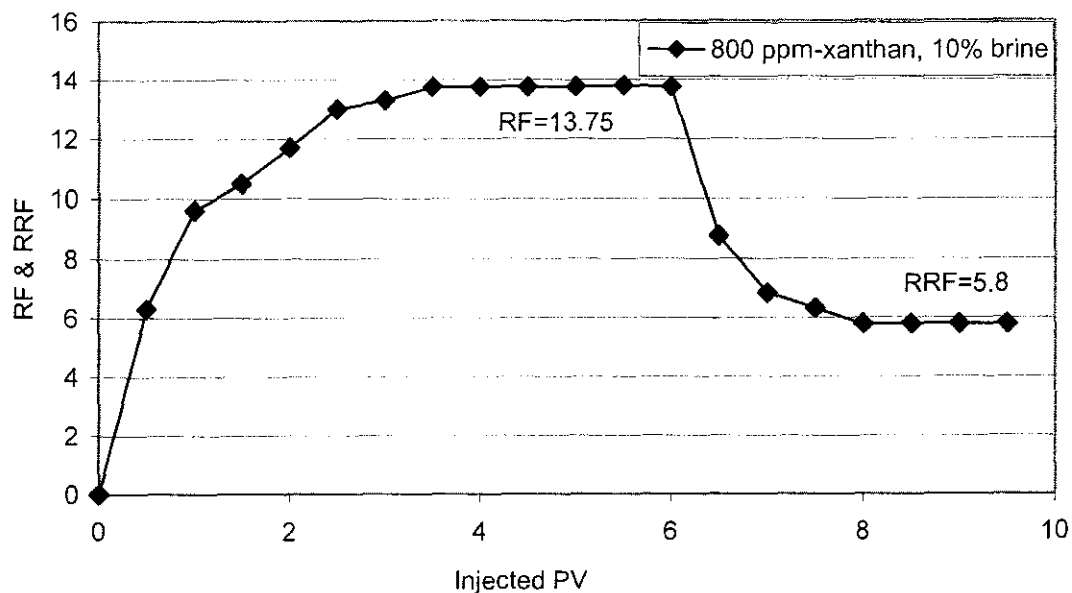


Figure 10. Resistance factor and Residual resistance factor using xanthan solution (core no. 4)

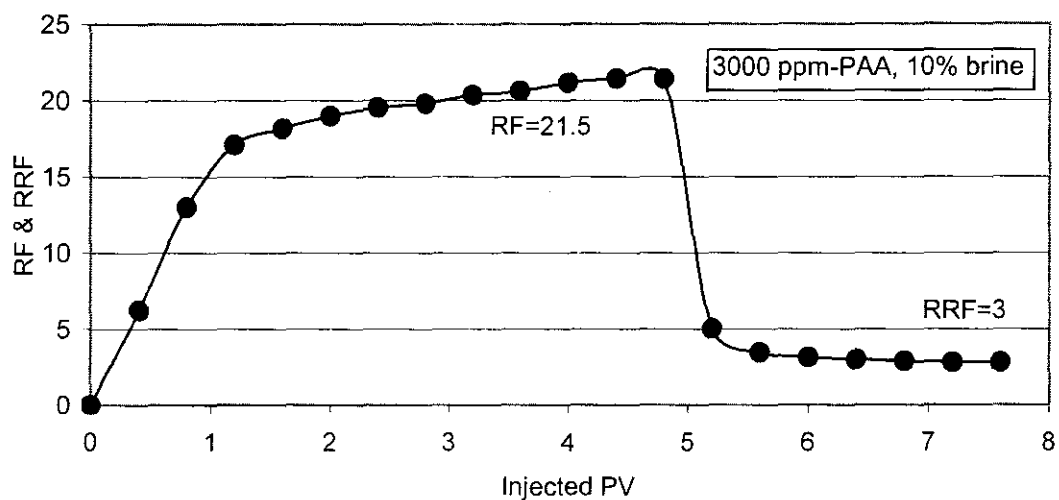


Figure 11. Resistance factor and Residual resistance factor using PAA solution (core no. 13)

Table 2. Comparison between RF & RRF for core samples flooded with xanthan solutions.

Core No.	RF	RRF	Concentration/Solution
1	61.7	29.1	1200 ppm/ 10%
2	46.6	16	1200 ppm/ 15%
3	12.75	7.14	800 ppm/ 15%
4	13.75	5.8	800 ppm/ 10%
5	23.1	12	800 ppm/ fresh water
6	18.4	2.3	1200 ppm/ fresh water
7	16	6	1200 ppm/ 20%
8	12	4	800 ppm/ 20%

Table 3 and Fig. 11 show the results of PAA solution: the higher is the polymer concentration, the higher are the RF and RRF for constant permeability. However, the values are lower than those obtained from xanthan solution. The comparison between the tested polymers based on the adsorption on the rock surface leads to the realization that the xanthan solution has better properties to be used in profile modification in high saline wells.

Table 3 Comparison between RF & RRF for core samples flooded with PAA

Core No.	RF	RRF	Concentration/Solution
9	12.6	3.1	1500 ppm/ 2.5%
10	16.5	6	1500 ppm/ 3.5%
11	33	15.06	2000 ppm/ 5%
12	48	21.9	3000 ppm/ 5%
13	21.5	3	3000 ppm/ 10%
14	27.1	2.4	2000 ppm/ 10%

4.2.1 Effect of Injection Rate

It is clear from the preceding results that shear rate affects the polymer solutions. In field application the shear rate is represented by an injection rate. Figs. 12 and 13 show RF function of flow velocity. Fig. 12 is for xanthan while Fig. 13 is for PAA. To get high value of RF it is recommended to have low injection rate of polymer solution. Increasing the flow rate reduces the RF as well as polymer adsorption and the permeability reduction will be low. This behavior strongly depends on the type of the polymer and its molecular weight.

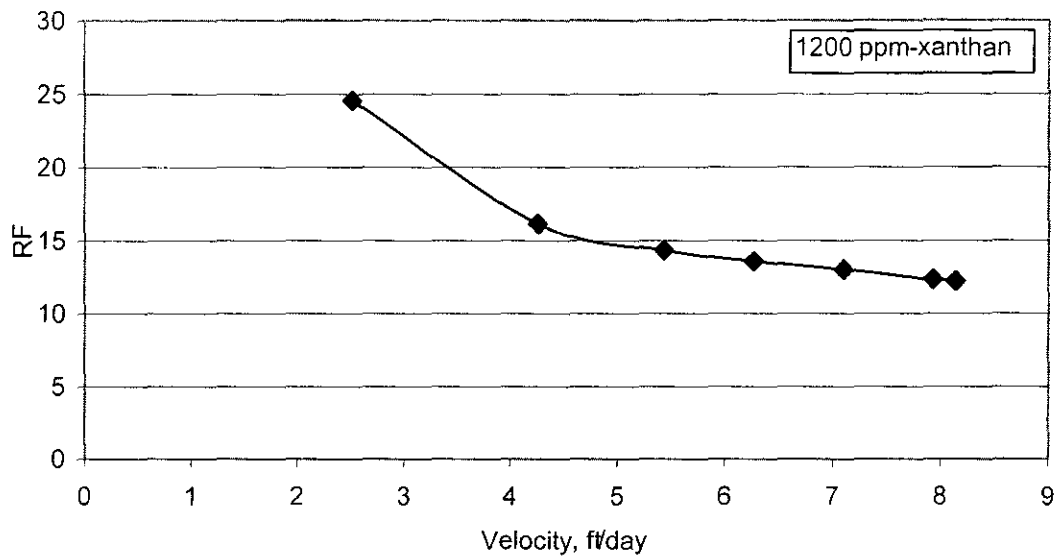


Figure 12. Resistance factor as function of velocity using xanthan solution (core no. 6)

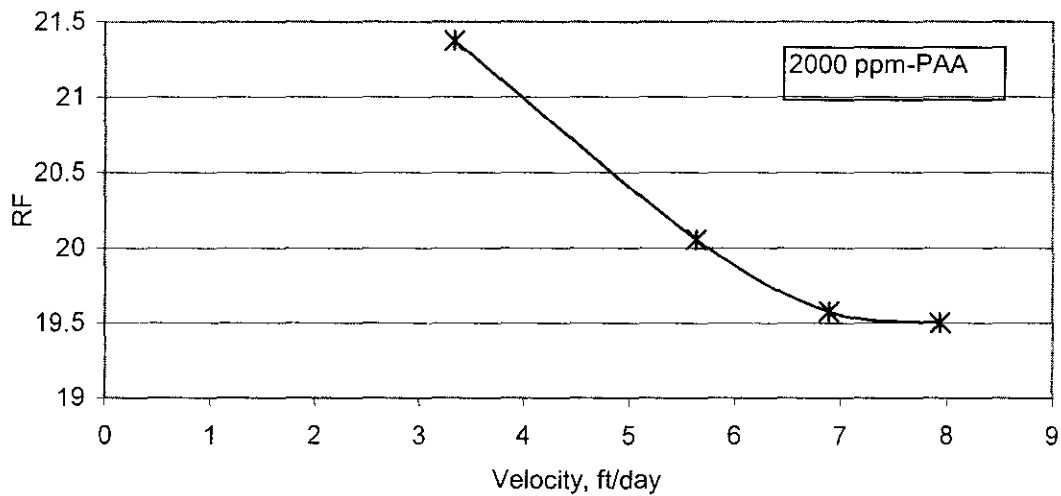


Figure 13. Resistance factor as function of velocity using PAA solution (core no. 14)

4.2.2 Effect of Rock Permeability

Different permeabilities are used for measuring the RF and RRF, Table 1. It can be seen from Tables 1, 2 and 3 that high permeability results in high RF and RRF. This indicates that the polymer adsorption on rock surface is high when the rock

permeability is high. Therefore higher reduction in rock permeability will be achieved.

4.2.3 Effect of Temperature

In order to investigate the effect of temperature on the selected polymer solution, the viscosity of 800 ppm and 1200 ppm of xanthan solutions were measured at a temperature of 52 °C. Temperature affects the stability of polymer solution by decreasing the solution viscosity. Fig. 14 shows a comparison between the viscosities of both solutions at temperatures of 25 °C and 52 °C at a shear rate of 14.7 s^{-1} . The viscosity of 1200 ppm xanthan solution dropped from 30 cp at 25 °C to 21.3 cp at 52 °C. For 800 ppm xanthan polymer solution the viscosity dropped from 15.5 cp at 25 °C to 9.25 cp at 52 °C.

To establish the effect of temperature on the adsorption on rock surface, experiments on core sample 7 & 8 were performed at a constant temperature of 52 °C with xanthan concentration of 800 ppm and 1200 ppm and 20% salinity. Fig. 15 shows the course of the RF and RRF as function of the injected pore volume (PV) for the core sample no. 7. In these experiments the maximum value of RF was achieved after injecting 6 PV of polymer solution instead of 4.5 PV at 25 °C temperature. This means that the top curve of RF is shifted forward. However, no significant change has been noticed in the value of RF and RRF at higher temperature.

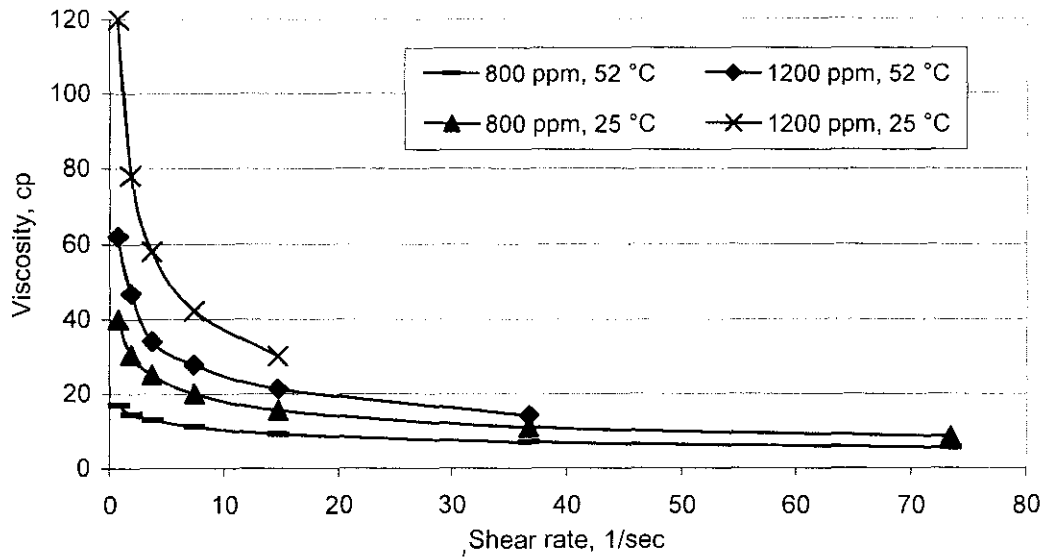


Figure 14. Viscosity of xanthan solution of different concentrations in 20% brine at 25°C and 52°C

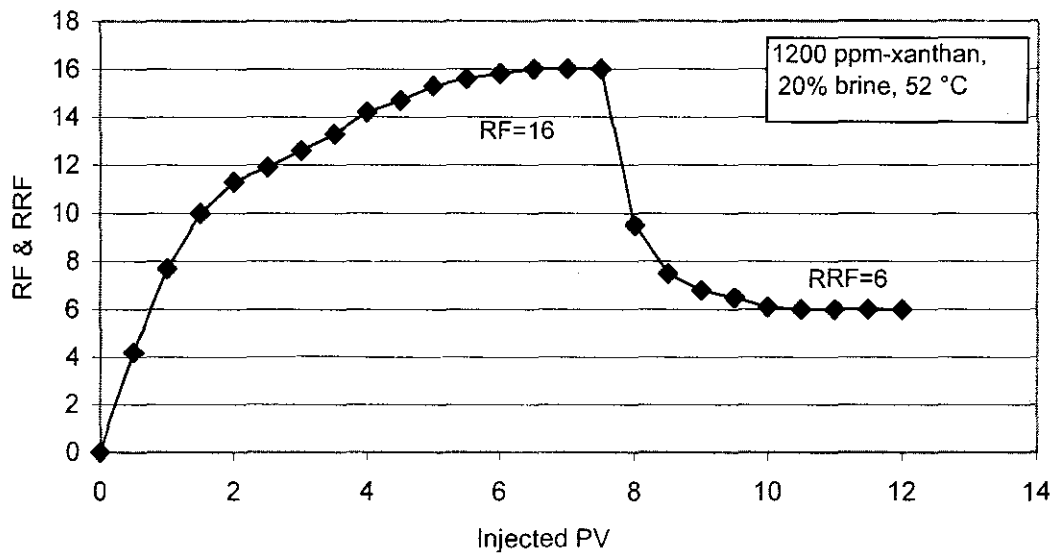


Figure 15. Resistance factor and residual resistance factor using xanthan solution (core no. 7)

5 Conclusions

The following conclusions are reached on the basis of the work conducted on xanthan and PAA polymer solutions:

1. The apparent viscosity of polymer decreases with increasing the salt concentration at any shear rate.
2. The apparent viscosity of polymer solution decreases with increasing the shear rate up to a certain value beyond which it becomes almost constant.
3. Xanthan has a great effect in reducing the heterogeneity of a reservoir due to the adsorption of the molecules on the core surface.
4. A reduction of permeability using polymer solution depends on the porous medium, the particular polymer used, the concentration of polymer, the salinity, and the injection rate.
5. Polyacrylamide (PAA) can reduce the heterogeneity in reservoir with low salt contents. High PAA concentration will be needed to tolerate the high salt content.
6. Partially reversible adsorption (physical) from the rock surface occurred by brine flooding (RRF).
7. The flooding velocity of polymer solution as well as the permeability has a great effect on the adsorption.
8. Temperature rise leads to delay the achievement of full adsorption on the rock surface. Therefore, more PV of the polymer solution is necessary
9. Xanthan can be recommended, as a good polymer candidate to be used in reservoirs with high salinity.

Received:

Symbols used

A	=	Cross section area of the core, cm ²
EOR	=	Enhanced Oil Recovery
k	=	Permeability, mD
L	=	Length of the core, cm
q	=	Flow rate, ml/hr
PAA	=	Polyacrylamide
ΔP	=	Pressure drop, psi
RF	=	Resistance factor
ΔP_p	=	Pressure drop during polymer flooding, psi
ΔP_w	=	Pressure drop during water flooding before polymer flooding, psi
RRF	=	Residual resistance factor
ΔP_{wa}	=	Pressure drop after polymer flooding, psi
ΔP_{wb}	=	Pressure drop during water flooding before polymer flooding, psi
WOR	=	Water Oil Ratio
λ_w	=	Mobility of water
λ_p	=	Mobility of polymer solution
μ	=	Apparent viscosity, cp

References

- [1] Kouznetsov, O.L.; Simkin, E.M.; Chilingar, G.V., and Katz, S.A.; *Journal of Petroleum Science and Engineering* 19 (1998) Elsevier Science, pp. 191-200.
- [2] Kerekes, F.; Kleinitz, W., and Jandl, A.; *Erdöl, Erdgas, Kohle Zeitschrift*, Juni 2000, pp. 292-296.

- [3] Ranjbar, M.; Schaffie, M., *Journal of Petroleum Science and Engineering* 26 (2000) Elsevier Science, pp. 133-141.
- [4] Ali, L.; Barrufet, M.A., *Journal of Petroleum Science and Engineering* 29 (2001) Elsevier Science, pp. 1-16.
- [5] Pusch, G.; Lötsch, Th., *Erdöl, Erdgas, Kohle Zeitschrift*, Juni 1997, pp. 272-277.
- [6] Zaitoun, A.; Kohler N.; and Marrast N., *In Situ* 14 (2) (1990), pp. 133-146.
- [7] Zaitoun, A.; Kohler, N.; Guerrini, Y., *Journal of Petroleum Technology* 6 (1991), pp. 862-867.
- [8] Dovan, H.T.; *SPE Paper 26603*, (1993), pp. 491-503.
- [9] Stanley, F.O.; Tanggu, P.S.; Mamoch, Ewen, *SPE Production and Facilities*, August 1997, pp. 181-186.
- [10] Prabuddaha Jain; Vinod Sharma; Raju A.V.; Patra, S.K., *SPE Paper 64437*, SPE Asia Pacific Oil and Gas Conference and Exhibition, Brisbane, Australia, 16-18 Oct. (2000).
- [11] Schlumberger WEC Emirates/Qatar, *Well Evaluation Conference*, Abu Dhabi, Nov. (1981), pp.57-88.
- [12] White, J.L.; Goddard, J.E.; Philips, H.M., *Journal of Petroleum Technology*, (Feb. 1973).
- [13] Lakatos L., et al., *Fourth European Symposium on EOR*, Hamburg (1987).
- [14] Omar, A.E., *SPE Paper 11503*, SPE Middle East Oil Technical Conference in Manama, Bahrain, 14-17 March (1983), pp. 509-512.