



UNIVERSIDADE ESTADUAL DE CAMPINAS SISTEMA DE BIBLIOTECAS DA UNICAMP REPOSITÓRIO DA PRODUÇÃO CIENTIFICA E INTELECTUAL DA UNICAMP

Versão do arquivo anexado / Version of attached file:

Versão do Editor / Published Version

Mais informações no site da editora / Further information on publisher's website: https://www.degruyter.com/view/journals/arh/29/1/article-p69.xml

DOI: 10.1515/arh-2019-0007

Direitos autorais / Publisher's copyright statement:

©2019 by De Gruyter. All rights reserved.

DIRETORIA DE TRATAMENTO DA INFORMAÇÃO

Cidade Universitária Zeferino Vaz Barão Geraldo CEP 13083-970 – Campinas SP Fone: (19) 3521-6493 http://www.repositorio.unicamp.br

Review Article

Mateus Ribeiro Veiga de Moura* and Rosângela Barros Zanoni Lopes Moreno

Concentration, Brine Salinity and Temperature effects on Xanthan Gum Solutions Rheology

https://doi.org/10.1515/arh-2019-0007 Received Mar 15, 2019; accepted May 16, 2019

Abstract: Xanthan gum is a biopolymer used in several different industries for a variety of applications. In the Petroleum Industry, xanthan gum has been applied in Enhanced Oil Recovery (EOR) methods for mobility control due to its Non-Newtonian rheological behavior, relative insensitivity to salinity and temperature compared to other conventional synthetic polymers, as well as its environmentally-friendly characteristics. As challenging reservoir conditions arise, candidate polymers should meet the screening factors for high salinity, high temperatures and heterogeneous reservoirs. This paper aims to evaluate the effects of temperature and monovalent salts on the rheological behavior of xanthan gum for Enhanced Oil Recovery purposes. We tested polymer solutions with brine salinities of 20,000/110,000/220,000 ppm of Sodium Chloride in a rheometer at temperatures of 23, 50, and 77°C. The results acquired showed that temperature plays a key role in viscosity and salinity protected the solution viscosity against negative thermal effects, unusually a turning point is observed where the increase in the monovalent salt content enhanced the polymeric solution viscosity. Such investigations coupled with a detailed discussion presented in the paper contribute to understand critical aspects of xanthan gum and its capability to provide basic requirements that fit desired screening factors for EOR.

Keywords: Xanthan Gum; Biopolymer; Rheology; Reservoir; EOR; High Temperature; High Salinity

PACS: 47.27.Ak, 47.10.ab, 47.80.-v, 36.20.-r

mateus.rvmoura@gmail.com

1 Introduction

In the petroleum industry, xanthan gum is widely employed in EOR and drilling applications [46]. Regarding the EOR methods, polymer flooding stands out as a chemical method for mobility control, where soluble polymers are added to the injection water to enhance oil displacement and sweep efficiencies of the reservoir [22]. Polymer flooding also delays the water breakthrough due to the lower volume of injection water needed to reach the residual oil saturation and because of the reduction in water relative permeability caused by polymer adsorption [25].

As more challenging reservoir conditions arise, more efficient and lower cost polymers are needed that meet the screening criteria. In conditions of high temperature, high salinity and very heterogeneous carbonate reservoirs, candidate polymers, especially biopolymers [3, 6, 7, 20, 32, 37] must provide the required rheology at minimum solution concentration. The polymer solutions also need to be thermally and mechanically stable and result in manageable adsorption on the formation rock.

The first step is a rheological assessment to design the target polymer solution to meet the screening factors for an EOR polymer flood project. Extracting data and information about the rheological behavior of the polymer solutions are essential to progressing to more detailed and complex evaluations and reservoir simulation.

Polymer solutions are classified as pseudoplastic fluids under most conditions. These types of fluids show a reduction of viscosity as shear rate increases. They are known as shear thinning fluids [44] and are represented by a curve with three distinct regions. The first region is a plateau characterized by a constant viscosity at very low shear rates or stress (η_0). The second region describes the shear thinning behavior, known as a pseudoplastic region. The third region is also a plateau and indicates the end of the pseudoplastic region and the beginning of the constant behavior of viscosity for high shear rates (η_{∞}).

There are several empirical models to describe the shear rate-dependence on viscosity [45], but the most commonly used is the power law relationship, also called Ostwald-de Waele model [2, 34], which describes the pseu-

^{*}Corresponding Author: Mateus Ribeiro Veiga de Moura: Universidade Estadual de Campinas Campinas, Brazil; Email:

Rosângela Barros Zanoni Lopes Moreno: Universidade Estadual de Campinas - Escola de Engenharia Mecânica – Departamento de Energia, Brazil

Open Access. © 2019 M. R. Veiga de Moura and R. B. Z. L. Moreno, published by De Gruyter.
Creative Commons Attribution 4.0 License

doplastic region.

$$\eta = K\gamma^{n-1} \tag{1}$$

where η is the apparent viscosity (cP), γ is the shear rate (1/s), *n* is the flow behavior index (dimensionless), and *K* is the consistency index (Pa·sⁿ). For pseudaplastic fluids, n < 1. The equation accurately describes only the pseudoplastic regime.

By plotting the polymer concentration against viscosity, it is possible to observe the transition between the dilute and the semi-diluted regime, which is called the critical concentration. These regimes express the degree of interaction between the macromolecules. In the semidiluted regime, the macromolecules are entangled, where the friction forces are imposed on each other, increasing the viscosity. In the diluted region, the macromolecules lie separated within the solution showing an independent behavior [1, 45].

The higher the polymer concentration in the solution, the higher the interaction between the polymer molecules and the solvent. As the polymer concentration decreases, the fluid solution loses its pseudoplastic characteristic resembling a Newtonian fluid, where the viscosity of dilute solutions presents negligible changes with shear rate increase [44]. Additionally, polymer concentrations for offshore field applications need to take into account the storage and processing capacity of the facilities. In such circumstances, the feasible range of concentrations lies between 500 ppm to 1200 ppm [10, 18, 50].

Xanthan gum is a polysaccharide, which is produced through fermentation of glucose or fructose by different bacteria [24]. Figure 1 shows the chemical structure of xanthan gum. The backbone structure of xanthan gum is similar to cellulose. The side chains of the polymer contain charged structures composed of acetate and pyruvate groups leading to a polyelectrolyte polymer.



Figure 1: Xanthan gum chemical structure. Figure by [49]

Xanthan gum has been modeled as a rigid-rod molecule [14, 47], comprising a helical structure where the side groups fold down along the helix creating a stiff rod-like macromolecule [30]. Holzwarth & Prestidge [17] and Holzwarth [15] say that the xanthan gum helix is composed of a single polysaccharide strand, while [41] indicates a double-stranded helix. Some other researchers assume different ordered configurations depending on salinity, temperature, and production origin [23, 29].

According to [13, 27, 41, 43], under high temperature, xanthan gum solution is subjected to a helix/coil transition or, also called, an order/disorder transition profile. This transition corresponds to the disruption of its structure, thus setting the molecule into a completely random coil conformation. The authors also showed in their studies that this relationship is also salinity dependent. Adding more salt to the solution yields a disordered conformation to an ordered and more rigid structure of the xanthan gum, meaning that low salinity polymer solutions exhibit a low transitional temperature and vice versa. Some xanthan gum in distilled aqueous solutions can reach this transition point even at room temperature [43]. In brines composed of divalent cations, this relationship tends to be more pronounced. Regarding molecular structure, the threshold temperature or so-called "melting temperature" is influenced by the acetate and pyruvate content [16].

Once the order-disorder transition point is achieved, the xanthan gum starts to behave as a Newtonian fluid, losing its ability to build viscosity entirely. At the region below the transition point, the xanthan gum in solution adopts a partial self-associated conformation due to polymer entanglements and hydrogen bonds that shows high viscosity at low shear-rates [38, 39]. This weaker structure partially breaks and the polymer chains are oriented under shear in a preferential direction towards the flow, showing a shearthinning behavior as the shear rate increases.

Temperature also plays a key role as regards viscosity, as it favors a progressive transition from partially ordered helix conformation to a random coil conformation. As a result, the xanthan gum becomes less viscous and less pseudoplastic until it reaches the Newtonian plateau. The molecules are abruptly rearranged into a fully random coil conformation, which dominates the rheological behavior [31, 35]. Several authors [8, 26, 52] documented that the relationship between the apparent viscosity of polymeric solution and temperature satisfies the Arrhenius equation:

$$\eta = A \exp\left(\frac{\Delta E_{\eta}}{RT}\right) \tag{2}$$

Test	Xanthan Gum Concentration (ppm)	Salinity (ppm)	Temperature (°C/°F)
01	10 - 5000	20,000	23/73,4
02	10 - 5000	110,000	23/73,4
03	10 - 5000	220,000	23/73,4
04	10 - 5000	20,000	50/122
05	10 - 5000	110,000	50/122
06	10 - 5000	220,000	50/122
07	10 - 5000	20,000	77/170,6
08	10 - 5000	110,000	77/170,6
09	10 – 5000	220,000	77/170,6

Table 1: Experimental conditions for rheological tests

where η is the apparent viscosity of the polymeric solution (Pa·s), A is a constant characteristic of polymeric solution (Pa·s). T is the absolute temperature (K), ΔE_{η} the viscous activation energy or the activation energy for flow (kJ/mol), and R is the universal gas constant (kJ·K⁻¹·mol⁻¹). The viscous activation energy is related to the dependence of the viscosity on temperature of the polymeric solution, higher viscous activation energy indicates greater influence of the temperature on the viscosity [42].

In summary, temperature combined with the brine salinity are triggers for the conformational transition and play a key role in the ability of the polymer solution to build viscosity, as illustrated in Figure 2. However, the xanthan gum response to ionic variation is unlike that of most other polyelectrolytes. Polyelectrolytes usually exhibit an expanded structure under conditions of low ionic strength, as the result of neighboring group electrostatic charge repulsion. The addition of salt results in a screening of the neighboring group repulsive forces and leads the molecule to collapse into a compact coil, reducing the intermolecular interaction, and thereby the viscosity.

Studies of the effects of salts on xanthan gum viscosity have produced contradictory results [51]. Some authors show that the thickness of dilute xanthan gum slightly increased in the presence of Sodium Chloride [11, 19, 33, 48, 51]. Dário *et al.* [5] suggest that increasing the concentration of soluble salts, decreases viscosity. However, a turning point is reached when very high concentrations of salt are incorporated into the solution, allowing the recovery of the ordered state conformance. Other authors show a moderate decrease in viscosity, less than other conventional polyelectrolyte structures [9, 12, 36, 40].



Figure 2: Xanthan gum conformance configuration under temperature and salinity effects. Modified from [49]

2 Methodology

The polymer used in this study is Xanthan gum obtained from *Xanthomonas Campestris* by **Sigma-AldrichTM**. According to [21], the average molecular weight is 2.65 Milion Daltons, the Pyruvate content is 0.9%, and the Acetate Content is 3.51%. A more detailed description of these measurements can be found in his paper.

The polymeric solution was prepared based on API-RP-63. Initially a stock solution of 5,000 ppm was prepared and the desired concentrations were obtained by diluting the stock solution. To make the Stock, dried polymer powder was uniformly sprinkled into the brine for 3 minutes. The polymeric solution was agitated for 9 - 12 hours and the magnetic stirrer was set to a medium degree of agitation to avoid powder clumping to ensure homogeneous solubilization. Finally, the solution was left overnight to hydrate.

Three different brine salinities composed of Sodium Chloride (*NaCl*) at three different temperatures were evaluated, as shown in Table 1.

The rheological tests were performed in a HAAKE MARS III® rheometer, which is a high precision instrument. The sensor used was the concentric cylindrical (DG41). The temperature control used was the THERMO HAAKE C25P refrigerated bath with a Phoenix II Controller. A new sample of solution was applied for each test.



Figure 3: Flow curves graph at 23°C and 20,000 ppm of NaCl



Figure 4: Flow curves graph at 23°C and 110,000 ppm of NaCl



Figure 5: Flow curves graph at 23°C and 220,000 ppm of NaCl

The flow curves were recorded at shear rates between $(10^{-1} \text{ and } 10^3) \text{ s}^{-1}$ with 20 measurement points. The acquisition mode was controlled by the shear rate.



Figure 6: Flow curves graph at 50°C and 20.000 ppm of NaCl



Figure 7: Flow curves graph at 50°C and 110,000 ppm of NaCl



Figure 8: Flow curves graph at 50°C and 220,000 ppm of NaCl

3 Results and Discussion

Figures 3-11 present the flow curves obtained during the experiments listed in Table 1. The Power Law model fitted the flow curves and Tables 3-11 list the parameters. For each

DE GRUYTER

condition, a clear pseudoplastic behavior is observed at polymer concentrations ranging from 5,000 – 2,000 ppm, comprising the semi-diluted region, and then a noticeable gap is observed between 2,000 ppm and 1,000 ppm. Concentrations below 1,000 ppm exhibit a slight pseudoplastic behavior and the initial viscosity plateau at low shear rates can be seen in the majority of the data. Figure 12 clearly shows that most curves lost the Non-Newtonian rheological behavior at concentrations around 500 ppm. The critical concentration was found at the intersection between a linear fitted curve within the 2,000 – 5,000 ppm concentration and a linear fitted curve within the 1,000

Table 2: Critical concentration

Salinity	Temperature	Critical Concentration
(PPIII)	((,)	(ppiii)
20,000	23/73.4	1313
110,000	23/73.4	1810
220,000	23/73.4	1916
20,000	50/122	1908
110,000	50/122	1941
220,000	50/122	1901
20,000	77/170.6	1912
110,000	77/170.6	1992
220,000	77/170.6	1995

Table 4: Fit parameters to the Power Law Model for 23°C/110,000	0
ppm NaCl	

Polymer	K	η	R ²
Concentration			
(ppm)			
10	1.2703	0.9900	0.3674
25	1.3333	0.9927	0.2686
50	1.4642	0.9899	0.5642
100	1.9002	0.9598	0.9923
200	3.2535	0.8984	0.9995
300	5.0065	0.8548	0.9967
400	7.7099	0.8066	0.9982
500	11.3035	0.7604	0.9990
600	15.2403	0.7339	0.9978
700	22.7513	0.6910	0.9990
800	27.9050	0.6677	0.9992
900	35.7632	0.6404	0.9995
1000	45.9374	0.6150	0.9993
2000	263.6323	0.4333	1.0000
3000	756.1088	0.3351	0.9999
4000	1521.7450	0.2798	0.9998
5000	2568.1000	0.2392	0.9998

Table 5: Fit parameters to the Power Law Model for 23°C/220,000ppm NaCl

 \mathbb{R}^2

0.3284

0.8912 0.8523

0.9930

0.9978 0.9945

0.9986

0.9992

0.9992

0.9991

0.9990

0.9993 0.9994

0.9999

0.9997

0.9997

0.9997

Table 3: Fit parameters to the Power Law Model for 23°C/20,000ppm NaCl

ppinnaet				Polymer	K	η
Polymer	K	η	R ²	Concentration		
Concentration		•		(ppm)		
(ppm)				10	1.6662	1.0020
10	1.2166	0.9886	0.5199	25	2.0927	0.9706
25	1.2166	0.9886	0.5199	50	2.1334	0.9875
50	1.3539	0.9796	0.8898	100	2.5438	0.9536
100	1.8715	0.9448	0.9285	200	4.4946	0.8845
200	3.6465	0.8674	0.9956	300	6.4309	0.8477
300	6.1025	0.8118	0.9977	400	9.1245	0.8094
400	9.1038	0.7698	0.9952	500	13.7438	0.7641
500	14.5849	0.7148	0.9989	600	18.9612	0.7281
600	20.5421	0.6795	0.9979	700	24.9744	0.6954
700	33.5204	0.6259	0.9989	800	35.4963	0.6583
800	40.8095	0.6058	0.9995	900	45.3467	0.6260
900	49.2111	0.5857	0.9995	1000	54.8477	0.6106
1000	64.5384	0.5568	0.9998	2000	280.7117	0.4416
2000	632.6263	0.3361	0.9999	3000	807.9335	0.3482
3000	1080.9600	0.2799	0.9999	4000	1657.7720	0.2892
4000	2038.6680	0.2219	0.9999	5000	3065.9400	0.2404
5000	3261.8590	0.1822	0.9999			



Figure 9: Flow curves graph at 77°C and 20,000 ppm of NaCl



Figure 10: Flow curves graph at 77°C and 110,000 ppm of NaCl



Figure 11: Flow curves graph at 77°C and 220,000 ppm of NaCl

– 10 ppm concentration (Table 2). The critical concentration increases sharply from the 23° C/20,000 ppm data and all the flow curves fall within the diluted region below the 2,000 ppm.



Figure 12: Viscosity versus Concentration at 7.0 1/s for all conditions



Figure 13: Viscosity versus Temperature at 7.0 1/s and 20,000 ppm of NaCl $% \mathcal{A}_{\mathrm{S}}$

The temperature showed a significant effect on the solution viscosity. All of the concentrations for each analvzed condition presented more than 60% reduction of its original thickness at room temperature (23°C). As seen in Figure 13, the increase in temperature linearly decreases the $\log \eta$. Figure 14 shows a plot of the measured points at 23°C and 77°C for each concentration, where the percentage of viscosity reduction caused by the increase in temperature was calculated (based on both temperatures, that is, how much of the viscosifying capacity of the xanthan gum at room temperature conditions decreased by the highest temperature measured). In the semi-diluted region, the viscosity reduction by temperature gradually decreased in higher salinities and in higher xanthan gum concentration. In solutions with higher salinities, the salt content protected the viscosity in the semi-diluted region; this is due to the salt content causing the molecules to form more ordered and rigid structures, avoiding thermal breakages

							2
Polymer	K	η	R ²	Polymer	K	η	R ²
Concentration				Concentration			
(ppm)				(ppm)			
10	0.6687	0.9969	0.0111	10	0.6687	0.9969	0.0111
25	0.6425	1.0066	0.1926	25	1.1389	0.9683	0.5701
50	0.8114	0.9772	0.7331	50	1.1448	0.9807	0.7548
100	1.0744	0.9582	0.8804	100	1.4420	0.9614	0.9944
200	1.7520	0.9193	0.9905	200	2.0512	0.9405	0.9950
300	2.7385	0.8859	0.9699	300	3.2940	0.8892	0.9992
400	4.1552	0.8455	0.9800	400	4.7305	0.8547	0.9987
500	6.1643	0.8117	0.9911	500	6.6533	0.8276	0.9967
600	9.1099	0.7651	0.9952	600	8.6672	0.8049	0.9927
700	12.8861	0.7358	0.9954	700	11.6596	0.7758	0.9939
800	16.2671	0.7138	0.9954	800	15.5267	0.7436	0.9971
900	21.7898	0.6880	0.9947	900	19.4756	0.7188	0.9969
1000	28.4430	0.6578	0.9970	1000	26.5003	0.6885	0.9974
2000	174.8925	0.4797	0.9993	2000	175.1305	0.4928	0.9995
3000	531.8956	0.3750	0.9996	3000	601.2938	0.3720	1.0000
4000	1280.5210	0.2909	0.9998	4000	1375.6650	0.2986	1.0000
5000	2229.3940	0.2474	0.9999	5000	2375.2150	0.2620	1.0000

Table 6: Fit parameters to the Power Law Model for $50^{\circ}C/20,000$ ppm NaCl

Table 8: Fit parameters to the Power Law Model for 50°C/220,000ppm NaCl

Table 7: Fit parameters to the Power Law Model for 50° C/110,000 ppm NaCl

Table 9: Fit parameters to the Power Law Model for $77^{\circ}C/20,000$ ppm NaCl

Polymer Concentration (ppm)	K	η	R ²	Polymer Concentration (ppm)	K	η	R ²
10	0.6816	1.0266	0.6151	10	0.3919	1.0302	0.6303
25	0.7082	1.0213	0.7897	25	0.3798	1.0592	0.7344
50	0.9007	0.9883	0.6455	50	0.5035	0.9805	0.8796
100	1.0057	0.9923	0.3693	100	0.6445	0.9798	0.8901
200	1.6685	0.9390	0.9983	200	1.0196	0.9456	0.9859
300	2.3079	0.9094	0.9971	300	1.7609	0.8888	0.9253
400	3.4364	0.8757	0.9912	400	2.6639	0.8431	0.9549
500	4.7421	0.8478	0.9877	500	3.3308	0.8560	0.8920
600	6.9620	0.8097	0.9927	600	4.8706	0.8222	0.9839
700	9.5146	0.7768	0.9940	700	6.3786	0.8005	0.9634
800	12.6283	0.7508	0.9935	800	9.1174	0.7572	0.9957
900	16.0176	0.7229	0.9966	900	10.1399	0.7742	0.9853
1000	21.1224	0.6941	0.9973	1000	14.6415	0.7218	0.9943
2000	139.7633	0.5052	0.9993	2000	99.6461	0.5229	0.9996
3000	451.9056	0.3929	0.9999	3000	292.0206	0.4482	0.9996
4000	1056.1910	0.3158	1.0000	4000	620.3818	0.3930	0.9993
5000	1963.8590	0.2649	1.0000	5000	1203.6250	0.3287	0.9997



Figure 14: Percentage reduction of viscosity of the solution measured at 20,000 ppm (NaCl) and 23°C, for all xanthan gum concentrations caused by the increase in temperature

and the disordered coil structures. Similar results were achieved by [4, 5, 43] however, in the diluted region, the influence of temperature on viscosity reduction remained constant, independently of the salt content and xanthan gum concentration. This observation suggests that the xanthan gum in such conditions is not capable of forming complex entanglements by interacting macromolecules on its conformance configuration, which are responsible for the pronounced Non-Newtonian behavior, thus their thermal disruption would lead to more severe viscosity reductions.

Analyzing the salinity effect (Figure 12), the increase in monovalent salt content from 20,000 ppm to 110,000 ppm showed a moderate to low reduction in the viscosity for a given temperature. However, the opposite behavior was observed when the salt content increased from 110,000 to 220,000 ppm, where the viscosity actually increased for a fixed temperature. The latter behavior has also been seen by previous works [11, 19, 33, 48, 51], even though it is not clear what mechanism drives this unusual effect (increase in viscosity with increasing salinity) within the range from 110,000 ppm to 220,000 ppm. The results obtained leads to a similar behavior described by [5], whereby extremely high salinity allowed the xanthan gum to recover its entangled partially ordered conformance, resulting in higher viscosities.

As regards the first step of addressing the screening criteria for a polymer flood project with respect to target solution, xanthan gum can build higher viscosities (with the same polymer concentration) than other high molecular weight synthetic polymers such as partially hydrolyzed polyacrylamide (HPAM). This also indicates that

Table 10: Fit parameters to the Power Law Model for 77°C/110,000)
opm NaCl	

Polymer	K	η	R ²
Concentration			
(ppm)			
10	0.4633	1.0238	0.7598
25	0.5059	1.0146	0.8240
50	0.5295	1.0132	0.3283
100	0.6749	0.9893	0.4442
200	0.9515	0.9517	0.9451
300	1.3942	0.9322	0.9895
400	1.9212	0.9067	0.9932
500	2.3375	0.9132	0.9716
600	3.6477	0.8527	0.9771
700	5.1042	0.8140	0.9787
800	5.5306	0.8514	0.9915
900	7.3635	0.8172	0.9919
1000	9.4668	0.7975	0.9729
2000	67.0745	0.6082	0.9970
3000	250.8032	0.4697	0.9994
4000	573.1118	0.4007	0.9998
5000	1170.2960	0.3399	0.9997

Table 11: Fit parameters to the Power Law Model for $77^{\circ}C/220,000$ ppm NaCl

Polymer	K	η	R ²
Concentration			
(ppm)			
10	0.6269	1.0011	0.2156
25	0.6883	0.9903	0.4420
50	0.7402	0.9931	0.4050
100	0.8136	1.0024	0.0271
200	1.2521	0.9571	0.9264
300	1.7297	0.9423	0.7687
400	2.2954	0.9330	0.9608
500	3.9109	0.8679	0.9618
600	4.8282	0.8687	0.9750
700	6.5213	0.8249	0.9984
800	7.2519	0.8386	0.9638
900	9.9391	0.8115	0.9695
1000	13.2971	0.7706	0.9976
2000	82.6556	0.6355	0.9879
3000	304.1791	0.4930	0.9969
4000	744.5516	0.4012	0.9990
5000	1573.5270	0.3234	0.9998

high salinity reservoirs mostly comprised of Sodium Chlorine could increase the xanthan gum viscosity over the long term due to the interaction between the injected brine and the reservoir brine.

However, xanthan gum also presented some important negative aspects that should be carefully evaluated before moving to further steps. A target viscosity of xanthan gum relies on shear rate, temperature, polymer concentration, and salinity. Literature suggests a feasible range of polymer concentration between 500 ppm to 1,200 ppm for offshore field applications. Concentrations above 1,200 ppm are prone to cause severe injectivity loss especially in tight formation because of its high viscosity. Concentrations below 500 do not show potential viscosities for Enhanced Oil Recovery, moreover a weak pseudoplacticity means an inefficient injectivity, since the shear-thinning effect is mild in the well vicinity. In summary a target solution in a rheometric test relies on shear rate, temperature, polymer concentration, and salinity. Simultaneously, for better injectivity, the solution should present the pseudoplastic behavior in ordered to thin in high shear rate regions close to the well and then recovering its target viscosity while flowing through the vast majority of reservoir under lower shear rates.

4 Conclusions

Xanthan gum presented a strong pseudoplastic behavior, especially in the semi-diluted region. Its ability to build viscosity in the diluted region (above 2,000 ppm) is significantly reduced when compared to the semi-diluted region (below 2,000 ppm) and a slight pseudoplastic behavior is observed. Most of the flow curves show a Newtonian behavior below 500 ppm of xanthan gum concentration leading to a narrow range of feasible concentrations for field applications in Enhanced Oil Recovery by polymer flood

Temperature is a very important parameter for the xanthan gum polymer solution as, for a fixed polymer concentration, viscosity decreases with the increase of temperature. Even though salinity also has an impact, its effect in reducing viscosity is smaller compared to that of temperature. It is important to note that a turning point within 110,000 - 220,000 ppm of *NaCl* range showed an opposite behavior where the increase in salinity increased the solution viscosity. Additionally, the salinity increase protected the xanthan gum in the semi-diluted region against the adverse impact of temperature on viscosity.

As regards the first step of addressing the screening criteria for a polymer flood project with respect to target solution, xanthan gum can build higher viscosities (with the same polymer concentration) than other high molecular weight synthetic polymers such as partially hydrolyzed polyacrylamide (HPAM). This also indicates that high salinity reservoirs could increase the xanthan gum viscosity over the long term due to the interaction between the injected brine and the reservoir brine.

The rheological assessment accomplished in this study reopens possibilities for xanthan gum applications for Enhanced Oil recovery under conditions found in the Brazilian pre-salt.

Acknowledgement: This research was carried out in association with the ongoing R&D project registered as ANP 20359-6, "*Injeção de Biopolímeros para a Recuperação Avançada de Petróleo de Reservatórios do Pré-Sal Brasileiro*" (Universidade de Campinas (Unicamp) / Shell Brasil / ANP) – Biopolymer Injection for Enhanced Oil Recovery in Brazilian Pre-Salt Reservoirs, sponsored by Shell Brasil under the ANP R&D levy as "Compromisso de Investimentos com Pesquisa e Desenvolvimento".

References

- [1] Al Hashmi A. R., Al Maamari R. S., Al Shabibi I. S., Mansoor A. M., Zaitoun A., Al Sharji H. H., Rheology and mechanical degradation of high-molecular-weight partially hydrolyzed polyacrylamide during flow through capillaries, Journal of Petroleum Science and Engineering, 2013, 105, 100-106.
- Bird R. B., Stewart W., Lightfoot E., Transport Phenomena, 1st ed., John Wiley & Sons, New York, 1960.
- [3] Bourdarot G., Ghedan S. G., Modified EOR Screening Criteria as Applied to a Group of Offshore Carbonate Oil Reservoirs, SPE Reservoir Characterisation and Simulation Conference and Exhibition (9-11 October, Abu Dhabi, UAE), 2011.
- [4] Choppe E., Puaud F., Nicolai T., Benyahia N., Rheology of xanthan solutions as a function of temperature, concentration and ionic strength, Carbohydrate Polymers, 2010, 82 4, 1128-1235.
- [5] Dário A. F., Lucas M. A., Hortêncio S. M. R., Neto J. C. Q., Petri D. F. D., The effect of calcium salts on the viscosity and adsorption behavior of xanthan, Carbohydrate Polymers, 2011, 84 (1), 669-676.
- [6] Davison P., Mentzer E., Polymer Flooding in North Sea Reservoirs, Society of Petroleum Engineers Journal, 1982, 22 (03).
- [7] Fournier R., Tiehi J.-E., Zaitoun A., Laboratory Study of a New EOR-Grade Scleroglucan, Society of Petroleum Engineers, SPE EOR Conference at Oil and Gas West Asia (26-28 March, Muscat, Oman), 2018.
- [8] Ghosh K., Maiti S.N., Melt Rheological Properties of Silver-Powder-Filled Polypropylene Composites, Polym. Plast. Technol. Eng, 1997, 36, 703–722.
- [9] Ghoumrassi-Barr S., Aliouche D., Characterisation and Rheological Study of Xanthan Polymer for Enhanced Oil Recovery (EOR) Application, Offshore Mediterranean Conference and Exhibition

(25-27 March, Ravenna, Italy), 2015.

- [10] Greaves B. L., Marshall R. N., Thompson J. H., Hitts Lake Unit Polymer Project, SPE Annual Technical Conference and Exhibition (16-19 September, Houston, USA), 1984.
- [11] Guo X. H., Li W. D., Tian J., Liu Y. Z., Pilot Test of Xanthan Gum Flooding in Shengli Oilfield, SPE Asia Pacific Improved Oil Recovery Conference (25-26 October, Kuala Lumpur, Malaysia), 1999.
- [12] Hamed S. B., Belhadri M., Rheological properties of biopolymers drilling fluids, Journal of Petroleum Science and Engineering, 2009, 67 (3–4), 84-90.
- [13] Holzwarth G., Conformation of the Extracellular Polysaccharide of Xanthomonas campestris, Biochemistry, 1976, 15 (19), 4333-4339.
- [14] Holzwarth G., Molecular weight of xanthan polysaccharide, Carbohydrate Research, 1978, 66 (1), 173-186.
- [15] Holzwarth G., Is Xanthan a Wormlike Chain or a Rigid Rod, Solution Properties of Polysaccharides, 1981, 2, 15-23.
- [16] Holzwarth G., Ogletree J., Pyruvate-free xanthan, Carbohydrate Research, 1979, 76 (1), 277-280.
- [17] Holzwarth G., Prestridge E. B., Multistranded helix in xanthan polysaccharide, American Association for the Advancement of Science, 1977, 197 (4305), 757-759.
- [18] Hryc A., Hochenfellner F., Best R. O., Maler S., Freedman P., Development of a Field Scale Polymer Project in Argentina. SPE Improved Oil Recovery Conference (14-18 April, Tulsa, USA), 2018.
- [19] Jang Y., Zhang H., Ke Chon, Bo Hyun, Choi H. J., Enhanced oil recovery performance and viscosity characteristics of polysaccharide xanthan gum solution, Journal of Industrial and Engineering Chemistry, 2015, 21, 741-745.
- [20] Jensen T., Kadhum M., Kozlowicz B., Sumner E. S., Malsam J., Muhammed F., Ravikiran R., Chemical EOR under Harsh Conditions: Scleroglucan as a Viable Commercial Solution, SPE Improved Oil Recovery Conference (14-18 April, Tulsa, USA), 2018.
- [21] Khouryieh H., Herald T. J., Aramouni F., Bean S., Alavi S., Influence of Deacetylation on the Rheological Properties of Xanthan–Guar Interactions in Dilute Aqueous Solutions, Journal of Food Science, 2007, 72, 173-181.
- [22] Lake L. W., Enhanced Oil Recovery, Facsimile ed., Enhanced Oil Recovery, Prentice-Hall, Englewood Cliffs, 1991.
- [23] Lecourtier J., Chauveteau G., Muller G., Salt-induced extension and dissociation of a native double-stranded xanthan, International Journal of Biological Macromolecules, 1986, 8 (5), 306-310.
- [24] Leela J. K., Sharma G., Studies on xanthan production from Xanthomonas campestris, Bioprocess Engineering, 2000, 23 (6), 687-689.
- [25] Littmann, W., Polymer Flooding, Developments in Petroleum Science, Elsevier, 1988.
- [26] Maiti S. N., Mahapatro P. K., Melt rheological properties of nickel powder filled polypropylene composites, Polym. Compos., 1988, 9, 291–296.
- [27] Milas M., Rinaudo M., Conformational investigation on the bacterial polysaccharide xanthan, Carbohydrate Research, 1979, 76 (1), 189-196.
- [28] Milas M., Rinaudo M., Investigation on Conformational Properties of Xanthan in Aqueous Solutions, Solution Properties of Polysaccharides, 1981, 3, 25-30.
- [29] Milas M., Rinaudo M., On the existence of two different secondary structures for the xanthan in aqueous solutions, Polymer Bulletin, 1984, 12 (6), 507-514.

- [30] Moorhouse R., Walkinshaw M., Arnott S., Extracellular Microbial Polysaccharides. ACS Symp. Ser., 1977, 45, 90-102.
- [31] Pelletier E., Viebke C., Meadows J., Williams P. A., A rheological study of the order-disorder conformational transition of xanthan gum. Biopolymers, 2001, 59, 339-346.
- [32] Quadri S. M. R., Shoaib M., AlSumaiti A. M., Alhassan S. M., Screening of Polymers for EOR in High Temperature, High Salinity and Carbonate Reservoir Conditions, (International Petroleum Technology Conference, 6-9 December, Doha, Qatar), 2015.
- [33] Rodrigues T. R., Palermo L. C. M., Cardoso L. V. S., Santos, I. C. V. M., Santos, A. S., Mansur, C. R. E., Polymers Rheological Behavior in Different synthetic Brines for EOR Application, Rio Oil&Gas Expo Conference, Instituto Brasileiro de Petróleo, Gás e Biocombustíveis (21-24 September, Rio de Janeiro, Brazil), 2018.
- [34] Reiner M., Deformation, Strain, and Flow, Interscience, New York, 1960.
- [35] Reinoso D., Martín-Alfonso M. J., Luckham P. F., Martínez-Boza F. J., Rheological characterisation of xanthan gum in brine solutions at high temperature, Carbohydrate Polymers, 03, 103-109.
- [36] Rinaudo M., Milas M., Polyelectroyte behavior of a bacterial polysaccharide from Xanthomonas campestris: Comparison with carboxymethylcellulose, Biopolymers, 1978, 17 (11), 2663-2678.
- [37] Rivenq R. C., Donche A., Nolk C., Improved Scleroglucan for Polymer Flooding Under Harsh Reservoir Conditions, SPE Reservoir Engineering, 1992, 7 (1), 15-20.
- [38] Rochefort W. E., Middleman S., Rheology of Xanthan Gum: Salt, Temperature, and Strain Effects in Oscillatory and Steady Shear Experiments, Journal of Rheology, 1987, 31 (4), 337-369.
- [39] Ross-Murphy S. B., Rheological Characterisation of Gels. Journal of Texture Studies, 1995, 26, 391-400.
- [40] Sandvik E. I., Maerker J. M., Application of Xanthan Gum for Enhanced Oil, Extracellular Microbial Polysaccharides, 1977, 19, 242-264.
- [41] Sato T., Norisuye, T., Fujita H., Double-stranded helix of xanthan in dilute solution: Evidence from light scattering, Polymer Journal, 1984, 16 (4), 341-350.
- [42] Samanta A., Bera A., Ojha K., Mandal A., Effects of alkali, salts, and surfactant on rheological behavior of partially hydrolyzed polyacrylamide solutions, J. Chem. Eng. Data, 2010, 55, 4315– 4322.
- [43] Seright R. J., Henrici B., Xanthan Stability at Elevated Temperatures, SPE Reservoir Engineering, 1990, 5, 52-60.
- [44] Sorbie K. S., Polymer-Improved Oil Recovery, 1st ed., Canada CRC Press-79, 1991.
- [45] Sorbie K. S., Polymer-improved oil recovery, 1st ed., Springer Science & Business Media., New York, 2013.
- [46] Standnes D. C., Skjevrak I., Literature review of implemented polymer field projects, Journal of Petroleum Science and Engineering, 2014, 122, 761-775.
- [47] Whitcomb P. J., Macosko C. W., Rheology of Xanthan Gum. Journal of Rheology, 1978, 22 (5), 493-505.
- [48] Whitcomb P. J., Ek B. J. Macosko C. W., Rheology of Xanthan Gum Solutions. Extracellular Microbial Polysaccharides, ACS Symposium Series, 1977, 45 (12), 160-173.
- [49] Xu L., Xu G., Liu L., Chen Y., Gong H., The comparison of rheological properties of aqueous welan gum and xanthan gum solutions, Carbohydrate Polymers, 2013, 92 (1), 516-522.
- [50] Yang G., Jiang R., Li X., Jiang Y., Evaluation of Polymer Flooding Performance Using Water-Polymer Interference Factor for an Offshore Oil field in Bohai Gulf: A Case Study, SPE Improved Oil

Recovery Conference (14-18 April, Tulsa, USA), 2018.

- [51] Zatz L., Knapp J. S., Viscosity of xanthan gum solution at low shear rates, Journal of Pharmaceutical Sciences, 1984, 73 (4), 468-471.
- [52] Zhou G., Willett J. L., Carriere C. J., Temperature dependence of the viscosity of highly starch-filled poly(hydroxy ester ether) biodegradable composites, Rheol. Acta, 2010, 39, 601–606.