Comparative study of stability of Guar gum using Nanoclay and Carboxyl Methyl Cellulose

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Abstract

Laboratory and field trials in polymer flooding revealed that one of the major challenges facing polymer flooding is the loss of polymer viscosity under challenging reservoir conditions such as high water salinity resulting in loss of the polymers viscosity and eventually reduction of the macroscopic sweep efficiency. Again, other challenges associated with use of Hydrolysed Polyacrylamide (HPAM) include difficulty in efficiently treating produced water from polymer flooding containing HPAM and also the low degradability of the HPAM solution making it difficult to meet discharge limit for disposal. Polymers like Guar gum and other polysaccharides are that biodegradable would suffice as better options with respect to environmental friendliness and stability.

This work investigates Guar gum solution at various concentrations and salinity as well as the effect of Nanoclay and Carboxyl methyl cellulose on the solutions viscosity, the rheological characterization of Guar solution showed that on increasing concentration, the viscosity of the solutions increased tremendously reflecting increasing intermolecular entanglement. Results revealed the effect of CMC was significantly different from that of Nanoclay; this improvement was attributed to the increased hydrogen bonds formed at molecular level. The analysis was also extended to determine the effect of salinity on the solutions, the result after 24hrs using CMC was still higher than Nanoclay despite the fact that CMC is anionic.

Keywords: Guar gum; CarboxylMethyl Cellulose (CMC); Polymer; Viscosity; Salinity.

Introduction

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Polymers must have the ability to maintain stability under challenging reservoir conditions like high salinity, high temperature during polymer flooding. However, the effect of attraction and repulsion of molecular charges are responsible for the resultant impact on solution's viscosity (Rellegadla 2017). HPAM is a commercial polymer used for polymer flooding and also a polyelectrolyte, as such when it interact with salt, there is a loss because of the negative charges on the polymer backbone chain which is signatured by effect of hydrolysis of the polyacrylamide molecule in order to reduce the effect of adsorption. (Don and green, 1996). HPAM and its derivatives have been used in most field applications than any other polymer in the area of polymer flooding, its advantages cut across its ability to viscosify at very little concentrations due to the fact that it can be synthesize to very high molecular weight of about 20million Daltons, its solubility in water, low cost and good physicochemical characteristics (Sun 2012; Changhong 2014). However, its inability to withstand high salinity restricts its use especially in offshore applications (Chang, 2011; Rellegadla 2017; Morel et al. 2008).

Field experience indicate that the major challenge facing polymer flooding is the inability of the polymers to maintain good viscosity under challenging reservoir conditions. For offshore fields, sea water is mostly available for preparing polymer solution prior to polymer flooding. Data from Dalia field (offshore) in Angola showed that Polyacrylamide (PAM) viscosity is decreased rapidly with increase in water salinity. The viscosity of the polymer decreases strongly when salinity increases from 25g/L to 40g/L. Mechanical degradation of surface facilities measured during tests via subsea well chokes ranges from 25 to 50% (Morel et al. 2008).

In China, research showed that polymer flood was cheaper than water flood, due to increased oil output and reduced costs in water injection and treatment (Cheraghian, 2015). At Daqing field (China), a field test was carried out in 1998 to investigate the effect of water salinity. Waste water with salinity of 3,800 ppm was used to prepare polymer solution. The tertiary recovery was much lower compared to adjacent areas flooded with less saline water (Wang et al.2002). Shengtuo field; one of the fields in Shengli oil field China, the polymer was mixed with produced water to save



fresh water resources. The salinity of fresh water was 680 mg/L, while that for the produced water was as high as 12,000 mg/L. It was observed that the polymer viscosity at injection wellhead dropped from 46 to 24 cp (Changhong 2014). At Chengdong field; also at Shengli Oil field China, HPAM solution was prepared with produced waste water to reduce cost from water treatment. From 2004 to 2005, the polymer solution maintained a viscosity around 20cp, but quickly declined to 1–5cp in 2006 after waste water was introduced.

Commercial polymers mostly used in chemical flooding are renewable polymers like xanthan gum and non-renewable polymers like partially Hydrolyzed Polyacrylamide (HPAM) and its derivatives. Polymer used in enhanced oil recovery are classified as polyacrylamide and polysaccharides. Polyacrylamide impact recovery by decreasing the mobility of the injected fluid in the reservoir and also decreasing the permeability of the reservoir rock; while polysaccharides are used to reduce the mobility of the injected fluid by increasing the viscosity of the fluid with very low levels of permeability reduction (Alquraishi 2011). Polysaccharides are renewable materials which make them viable biopolymers for viscosity enhancement due to their low cost, strong resistance to mechanical and thermal degradation, biopolymers in the industry include xanthan gums, hydroxyethyl cellulose, guar gum, carboxyl methyl cellulose (Alquraishi 2011).

Guar gum is the endosperm polysaccharide of *Cyamopsis tetragonolobus*, It grows naturally in India and Pakistan. Guar gum is processed from the seed of the guar plant, Cyamopsis tetragonolobus is a branched copolymer based on its structure. Grinding the endosperm of the guar bean seeds produces averagely pure guar gum. The backbone of the polymer is composed of mannose chains, each mannose unit has a galactose branch bonded to it in the ratio of 2:1. The two monomers: Mannose and Galactose are simple sugars that defines the gum as a "galactomannan" (Chatterji 1981; El-Daw 1994). Guar gum is non-ionic and provides thickening and increasing viscosity in aqueous solutions (El-Daw 1994; Eiroboyi 2018).

Cellulose is the most abundant natural polymer, its derivatives is less expensive and is used for various field applications. Its derivatives like Carboxymethyl cellulose (CMC) is the most common and cheapest cellulose derivative, it is well known as a safe, biodegradable material, which is widely used as food, cosmetic and pharmaceutical additives etc. It is an anionic and water-soluble natural polymer derivative (Yu 2009). It is widely used in detergents, oil exploration, food applications, paper and textile industries due to its high viscosity. The addition of CMC to the cassava starch films causes increased tensile strength and reduced elongation at break of blended films. This was attributed to the good interaction between cassava starch and CMC (Ibrahim 2007). CMC and Gum Arabic have several hydroxyl groups in their structure such that when blended, hydrogen–bonding interactions between them are expected to occur. As a result, thermal and mechanical properties could be improved (Ibrahim *et al* 2014).

The properties of injected polymer play an important role in the overall success of polymer flood projects. The chosen polymer must meet a few requirements including good solubility in water and good injectivity. Moreover, polymer must maintain a relatively high viscosity under the effect of temperature, shearing, water salinity, and hardness (Changhong 2014). With this in mind, there is need to increase the resistance of the polymer against the effect of high salinity, this work analysed the rheology of Guar gum solution with nanoclay and CMC at various concentrations.

METHODOLOGY

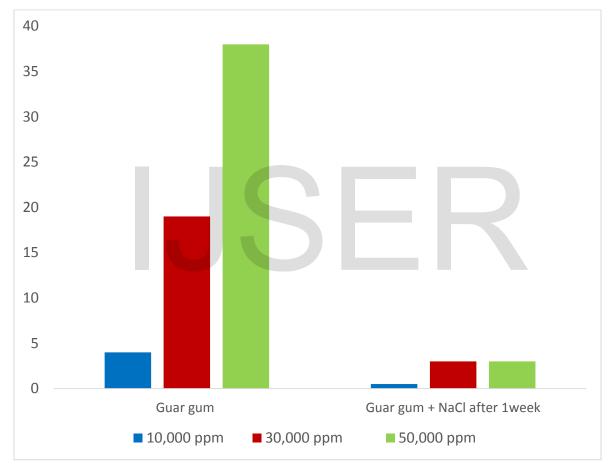
In this analysis, Nanoclay and CMC were equally used as an additives to modify the properties of Guar gum (yellowish). 5g of CMC and of 8g of Nanoclay was used to modify the rheology of Guar gum solution. The rheological properties were measured using Ofite Viscometer at 600, 300, 200, 100, 60, 30, 6 RPM; this viscometer has dial readings up to 330cp.

Experimental Procedure

Laboratory work was conducted to characterize the polymer using different concentrations of polymer solutions from 10,000ppm, 30,000ppm to 50,000ppm which



was prepared by dissolving them in water; the solution was stirred until mixtures were homogenous. and after which the Guar gum solutions was allowed to stand for a period of 24 hours and then the rheology of the gums without NaCl was carried out using Ofite Viscometer at seven different speeds, this procedure was repeated for another 24hrs with the added additives to determine the rheology with NaCl and eventually repeated after 1 week to determine the stability of the polymer with respect to salinity.



RESULTS AND DISCUSSION

Figure 1: The Effect of increasing concentration of Guar gum based on salinity after 1week

The increased viscosity as concentration is increased is born from the fact that the polymer is a galactomannan with molecular ratio of the mannose: galactose of 2:1 as such upon hydration, there is increased interaction between the molecular bonds of the polymer chains leading to increased electrostatic repulsion. However, the effect of

salinity on the polymer was very obvious after 1 week, this is because of the fact that the polymer chains have been scission which could have been as a result of the effect of oxidation, the effect of salinity though guar gum is non-ionic and also as a result of the effect of mechanic degradation. According to Chatterji et al (1981), Guar gum is very susceptible to shear degradation. Figure 1 and table 1 show that there is reduction in the viscosity after 1 week.

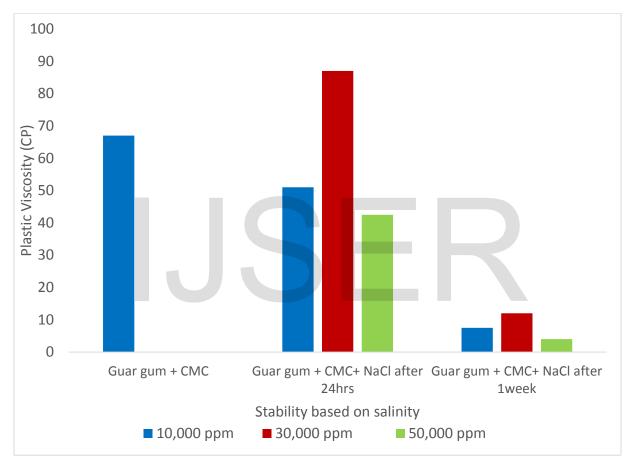


Figure 2: The Effect of CMC on increasing concentration of Guar gum based on salinity after 24hrs and after 1week

There was synergy between the molecular chains of guar gum and CMC, this is evident from the increased viscosity as given in Table 2 when compared to table 1 which is synonymous with the increase from 4cp to 67cp. This increased synergy could be related to the formation of increased bonds between the guar gum molecular chains and the CMC polymer, the Guar gum polymer displayed the ability to interact with other



polysaccharides because of the nature of its molecular structure. It has substituted and un-substituted regions (Garcia-Ochoa 2000; Mathur 2005; Doublier 1981; Dea 1977), these un-substituted regions give room for interaction with polysaccharides like the CMC and eventually increased the hydrogen bonding present in the solution.

Again in the face of salinity, given the fact that Guar gum is a non-ionic polymer, for 10000ppm, there was a loss of about 24% after 24hrs. Equally, the polymer solution experience a loss of about 89% loss after 1week. These losses can be ascribed to the fact that CMC is anionic and Guar gum is non-ionic. It means that the presence of the anions alongside the cations of NaCl caused an interaction that resulted in the shielding of the ions of CMC polymer reflecting a decrease in solution viscosity as can be seen from the Figure 2.

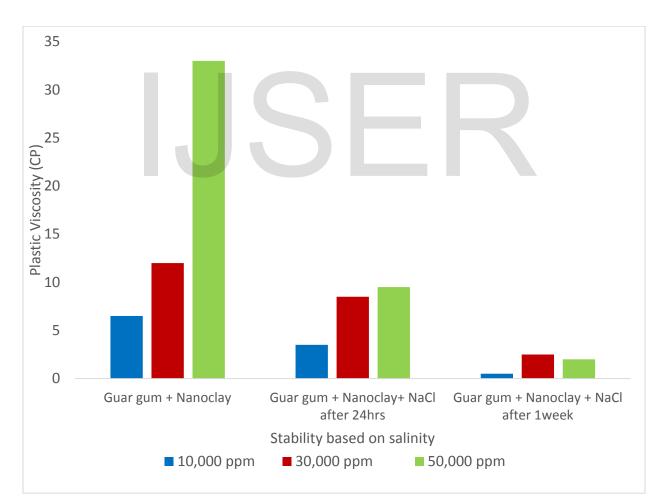


Figure 3: The Effect of Nanoclay on increasing concentration of Guar gum based on salinity after 24hrs and after 1week



From Figure 3 and table 3, the increased viscosity for 10000ppm based on the effect of Nanoclay resulted in an increase from 4cp to 6.5cp which is about 62.5%, this increase in viscosity could be related to the formation of hydrogen bonds between the oxygen atom of the clay and hydrogen atoms of Guar gum. Nevertheless, in the area of stability with respect to salinity, the 10000ppm reflected a drop of about 46% after 24hrs and 92% after a duration of 1week.

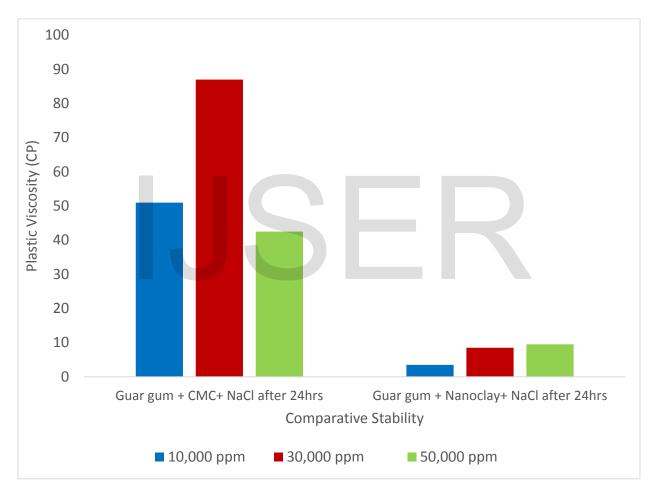


Figure 4: Comparative stability Analysis between CMC and Nanoclay after 24hrs

Stability between Guar gum with CMC resulted in greater stability than Guar gum with Nanoclay even though CMC is anionic, the resultant effect from CMC gave still far better stability than Nanoclay after 24hrs as is evident from Figure 4. After a period of

758

1week, the presence of CMC resulted in still far much higher stability than the presence of Nanoclay as shown in Figure 5.

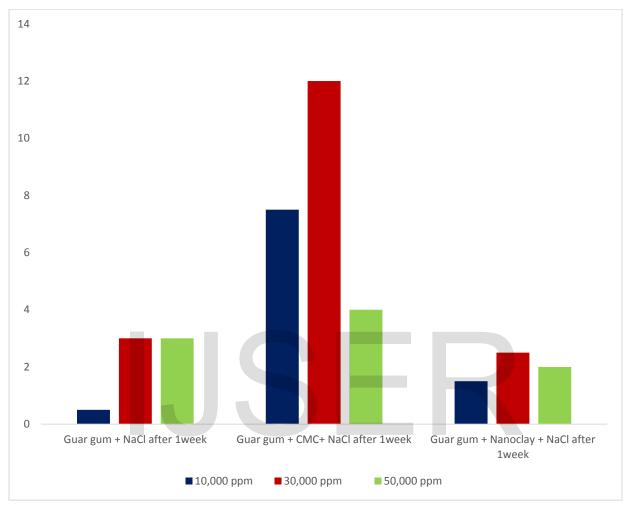


Figure 5: Comparative stability Analysis between CMC and Nanoclay after 1week

Conclusion

- 1. The rheology of Guar gum show synergy more with CMC than with Nanoclay as can be seen from the resultant viscosity with the use of CMC.
- 2. The stability of the Guar gum with the use of CMC was low and especially with the use of Nanoclay, this is related to the fact that CMC is anionic as such reaction with the cations of NaCl resulted in decreased electrostatic repulsion of the polymer chains and subsequent scission of the polymer chains.

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- 3. The resistance provided by Guar gum solutions was much greater at 30000ppm than at any other concentration. It signifies that not in all cases that increasing concentration of polymer solution will always yield increasing stability.
- 4. The stability after a longer duration decrease subsequently compared to the stability for a shorter duration. The longer the effect of salinity, the lower the stability.

NOMENCLATURE

- CMC CarboxylMethyl Cellulose
- HPAM Hydrolysed Polyacrylamide
- NaCl Sodium Chloride Salt
- PPM Parts per million
- CP Centipoise

References

- 1. Alquraishi, A. A. and Alsewailem, F. D. Adsorption of Guar, Xanthan and Xanthan-Guar mixtures on high salinity, high temperature reservoirs. king abdulaziz city for science and technology, 2011
- Chang H. G. Scientific research and field applications of polymer flooding in heavy oil recovery J Petrol Explor Prod Technol (2011) 1:65–70 DOI 10.1007/s13202-011-0014-6
- Changhong G. Shi J. Zhao F. Successful polymer flooding and surfactant-polymer flooding projects at Shengli Oilfield from 1992 to 2012 (2014) DOI 10.1007/s13202-013-0069-7
- 4. Chatterji J. and Borchardt J. Applications of water-soluble polymers in the oil field. J Pet Technol 33:2,042–042,056. (1981). doi:10.2118/9288-PA
- Cheraghian G."Effects of nanoparticles on wettability: A review on applications of nanotechnology in the enhanced Oil recovery", Young Researchers and Elite Club, Omidieh Branch, Islamic Azad University, Omidieh, Iran, 2015

- Doublier J. L. and Launay B. Rheology of Galactomannan Solutions: Comparative Study of Guar Gum and Locust Bean Gum. Food Science Department, France, 1981
- Eiroboyi, I. and Ikiensikimama S. S. Improved Water Soluble Polymers for Chemical Flooding, SPE 193489, Presented at *Nigeria Annual International Conference and Exhibition*, Lagos, Nigeria 6-8 August, 2018.
- 8. El-Daw G. A Study of Guar Seed and Guar Gum Properties (Cyamopsis tetragonolabous). Faculty of Agriculture, University of Khartoum, 1994.
- Guo X. H., Li D. W., Tian J., Liu Y. Z. Pilot test of xanthan gum flooding in Shengli oilfield". In: SPE 57294 presented at SPE Asia Pacific improved oil recovery conference, (1999) Kuala Lumpur.
- Marthur V. and Mathur N. K. Fenugreek and other lesser known legume galactomannan -polysaccharides: Scope for development. *Journal of scientific and Industrial research*, Vol 64, July 2005, pp 475 to 481
- 11. Martins F.D. Mechanical Degradation of Polyacrylamide Solutions in Core Plugs from Several Carbonate reservoirs, Paper SPE 12651 presented at the 1984 SPE/DOE symposium on Enhanced Oil Recovery, Tulsa, April 15-18
- Morel D. Vert M. Jouenne S. and Nahas E. Polymer injection in deep offshore field: the Delia Angola case. SPE 116672 presented at SPE annual technical conference and exhibition, Denver, Colorado, 21–24 September, 2008.
- Rellegadla S., Prajapat G., and Agrawal A., (2017), Polymers for enhanced oil recovery: fundamentals and selection criteria. Appl Microbiol Biotechnol, DOI 10.1007/s00253-017-8307-4.
- 14. Sun Y. Saleh L. and Bai B. Measurement and Impact Factors of Polymer Rheology in Porous Media *Petroleum Engineering Program, Missouri University of Science and Technology*, Rolla, Missouri, USA. 2012
- Wang D, Cheng J, Wu J, Wang Y (2002) Producing by polymer flooding more than 300 million barrels of oil what experiences have been learnt. SPE 77872 presented at Asia Pacific oil and gas conference and exhibition, Melbourne, Australia, 8–10 October 2002

Yu L. Biodegradable Polymer blends and composites from renewable resources.
 A John Wiley and sons Inc., Publication, 2009

Table 1: Rheological Properties of Guar gum before and after the effect of NaCl(Rheology of the gum without any additives)

	Viscosity be	fore the effe	ect of salinity	Viscosity after	the effect of	salinity for I	
RPM	(cp)			week (cp)			
	10,000	30,000					
	ppm	ppm	50,000 ppm		30,000		
	without	without	without	10,000 ppm +	ppm +	50,000 ppm	
	NaCl	NaCl	NaCl	NaCl	NaCl	+ NaCl	
6	0	4	9	0	1	1	
30	0	11	30	0	1	1.2	
60	2	17.5	47	0	1.5	1.5	
100	3	19	65	1	2	2.0	
200	5	31	93	1.5	3	4.5	
300	7	39	113	2	4	5	
600	11	58	151	2.5	7	8	

 Table 2: Rheological Properties of Guar gum and CMC before and after the effect of NaCl (the effect of CMC)

RPM	Viscosity before the effect of salinity (cp)			Viscosity after the effect of salinity for 24hrs (cp)			Viscosity after the effect of salinity for 1 week (cp)		
	10,00	10,00 30,00		10,000	30,000	50,000	10,00	30,000	50,000
	0 ppm	0 ppm	0 ppm	ppm	ppm	ppm	0 ppm	ppm	ppm
6	19	58	116	6	17.5	5.5	1	1	1
30	62	155	254	25	58	19	2	2	1
60	93	213	330	41	93	33	3	3	1.5
100	127	245	330	60	127	49	5	5	2

200	180	320	330	95	188	55	10	9.5	3.5
300	214	330	330	122	237	72.5	14.5	13	5
600	281	330	330	173	324	115	22	25	9

 Table 3: Rheological Properties of Guar gum and Nanoclay before and after the

 effect of NaCl (the effect of Nanoclay)

	Viscosit	y with	n the	Viscosit	y with	n the	Viscosit	y with	n the
	addition of Nanoclay		addition of Nanoclay		addition of Nanoclay				
	before the effect of			after the effect of salinity			after the effect of salinity		
RPM	salinity (cp)			for 24hrs (cp)			for 1 week(cp)		
	10,000	30,000	50,000	10,000	30,000	50,000	10,000	30,000	50,000
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
6	1	2.5	5	1	1.5	1.5	1	1	1
30	1.5	4.5	19	1	2.5	2.5	1	1	1
60	2.5	7.5	31	1.5	3.5	3.5	1	1.5	1.5
100	3	11	44	2	5	5.5	1.5	1.5	1.5
200	4	17	67	3	8	8	2.5	2	2.5
300	6.5	22.5	84	5	11	11	2.5	2.5	3
600	13	34.5	117	8.5	19.5	20.5	3	5	5