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Effects of Nanoparticles in Polymer-Based Enhanced Oil Recovery Technique

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Polymer-based chemical enhanced oil recovery methods, while overcoming the disadvantages of conventional waterflooding such as viscous fingering, have performance issues in saline and high temperature conditions that can be addressed through the application of nanotechnology. In the present work, a nanofluid prepared from copper oxide (PHPA) is explored in order to improve the oil recovery efficiency. The prepared nanofluid is analyzed for its rheological performance at various additive concentrations, salinities and for temperatures ranging from 25 to 100 °C. The analysis predicts the nanofluid to exhibit a significant improvement in its rheological properties with resistance to saline and temperature conditions.

Keywords: Enhanced oil recovery, Chemical, Polymer, Rheology, Nanotechnology.

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1. INTRODUCTION

Oil and gas industries are the top listed players in feeding energy to this world for many decades and expected to hold the same position at the current oil production rate. Thus, the discovering and exploiting of new sources of hydrocarbons for boosting hydrocarbon production were the focus of oil and gas companies. Usually, available natural energy aids in the production of one third of hydrocarbon production. With further elapse of time, the pressure depletion causes a reduction in production. Therefore, secondary methods such as water flooding have emerged to extract the remaining available oil. The water flooding method usually deals with the recovery through injection of high-pressure water with some additives into the reservoir. Water flooding is very cheap, especially in offshore operations, due to the availability of water [1]. However, only 10-15 % of the remaining oil could be recovered, leaving behind 45-55 % of oil in the reservoir, owing to viscous fingering mechanism of the water flooding method [2]. Thus, while extracting the remaining oil, the researchers proposed an alternative and effective tertiary recovery method, namely Enhanced Oil Recovery (EOR) method.

There are three types of EOR methods, namely the miscible gas injection, thermal methods, and chemical flooding. The miscible gas injection methods improve microscopic displacement efficiency by reducing IFT between oil and displacing fluid. The drawback of this method is that gas used (especially nitrogen and carbon dioxide) is very less viscous and less denser as compared to oil, hence causes viscous fingering and thereby affects the overall efficiency [1]. Thermal methods use a heat source to increase the reservoir temperature and, as a result, oil viscosity decreases, thereby enhancing the heavy oil production uses [3]. Steam flooding and In-Situ Combustion (ISC) [4, 5] are the widely used methods under this category.

Chemical flooding uses any or combination of polymers, surfactants (surface acting agents) and alkaline agents to improve oil recoveries. Polymer flooding is the most reliable and highly adopted chemical [6, 7]. The method overcomes the disadvantages of conventional water-flooding such as viscous fingering. The mechanism of polymer flooding can be understood by the mobility ratio (M) property, defined as the ratio of mobility of displacing phase to mobility of displaced phase. As the viscosity of the water increases, the mobility ratio M decreases, promoting the oil production [8]. Partially hydrolyzed polyacrylamide (PHPA) polymer is the commonly used chemical in polymer flooding due to its physiochemical and low-cost characteristics [9]. However, at high temperature conditions, the amide group of PHPA is reported to transform to carboxylic acid through extensive hydrolysis and it at high saline conditions would come into contact with cations to precipitate when it is commonly present in reservoir brines, limiting its application [10, 11]. Further, PHPA acts as a shear thinning-polymer, and when subjected to high shears, its chains get cutoff causing a reduction in its viscosity [12]. This limitation of PHPA can be overcome by nanotechnology owing to the fact that nanoparticles exhibit better thermal stability at elevated reservoir temperatures [13, 14].

The research work in the area of nanotechnology was started way back in 1980s. Though a variety of nanoparticles (NPs) have been synthesized [15], their application in petroleum exploration and production is less studied. Some researchers have explored the nanofluid application in improving drilling fluid characteristics [16, 17]. Further, NPs are reported to contribute to wettability alteration and Interfacial Tension (IFT) reduction in EOR process. In this context an

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attempt has been made to explore the effect of copper oxide (PHPA) based nanofluid in enhancing the oil recovery performance.

2. MATERIALS AND METHODS

2.1 Materials

PHPA polymer was gathered from ONGC, India. Nanoclay (size), nano copper oxide (size) of synthesis grade. and laboratory grade potassium chloride (KCl) were purchased from Sigma Aldrich, Mumbai, Mahrashtra, India. Distilled water was used in the present work.

2.2 Preparation of Nanofluids

Initially, 1 g of PHPA and 2.5 g of KCl were mixed in 100 ml of distilled water to prepare a polymer base fluid named as B1. The base fluid was then mixed with 0.5 g of nanoclay named as NF1. This solution was further mixed with 0.25 g of nano copper oxide (N-CuO) and named as Nano-Fluid-2 (NF2). All the prepared solutions were kept on a magnetic stirrer for 16 h at standard conditions. Further, the ultrasonic bath was employed to assure the complete dissolution of additives in the solutions. The exact concentrations of additives used in this study are detailed in Table 1.

Table 1 – Composition of the polymer solution and nanofluids used in the experiments

Constituents	Base fluid (B1)	Nano-fluid 1 (NF1)	Nano-fluid 2 (NF2)
Water (ml)	100	100	100
PHPA (g)	1	1	1
KCL (g)	2.5	2.5	2.5
Nanoclay (g)	–	0.5	0.5
Nano copper oxide (g)	–	–	0.25

2.3 Rheological Study

The rheology of displacing fluids is one of the most important parameters which ensure the optimization of displacement efficiency inside the reservoir when using polymer based EOR technique. The apparent viscosity of polymer solutions is significantly sensitive to the shear rates and temperature. The above-mentioned sensitiveness refers the polymeric displacing fluids as non-Newtonian fluids, whose rheology is described by the model. A widely used model for polymer-based displacing fluid is the power law model, which is described as:

$$\zeta = k\gamma^{n}. \qquad (1)$$

Rheological property of interest i.e., apparent viscosity of the prepared solutions, was analyzed using Anton Par rheometer at varying shear rate i.e., 1 to 1000 s^{-1}. Prior to analyze the rheological data, the prepared base fluids were aged at ambient condition for 24 h to ensure the mechanical stability of solutions. Further, the salt tolerance property was analyzed by varying the temperature from 25 to 100 °C.

3. RESULTS AND DISCUSSION

3.1 Rheological Analysis of Nanofluids

Initially, the prepared base solutions B1, NF1 and NF2 were aged for 10 h and the shear behavior at a varying shear rate (20 to 1000 s^{-1}) was measured under ambient conditions and is shown in Fig. 1. It can be observed from Fig. 1 that viscosity sharply decreased with increasing shear rate. However, viscosity declination is lower for NF2 (51-8.5 mPa·s) than for both NF1 (31 to 4.5 mPa·s) and B1 (29-1.2 mPa·s) prepared with conventionally used PHPA polymer. Thereby, the base fluid prepared using copper oxide incorporating PHPA and nanoclay i.e., NF2 showed superior shear resistance properties compared to B1 (prepared with PHPA only) and NF1 (formulated with a combination of nanoclay and PHPA), as depicted in Fig. 2. The superior performance of the NF2 formulation at shear rates can be attributed to the intra/inter-molecular interaction between nanoclay and PHPA in the presence of CuO. Oil reservoirs with high pressure injection can exert higher shearing, which might affect the polymer chains to degrade causing the EOR project unfeasible. Thereby, it is important to consider the chemical slugs like NF2 that withstand even higher shear conditions.

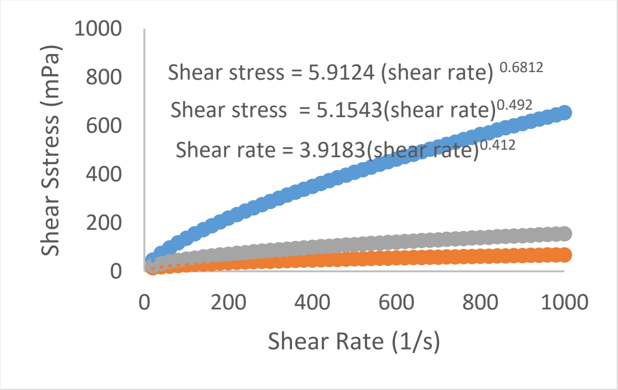

Fig. 1 – Shear stress vs shear rate relation of the nanofluids

Table 2 – Power law model parameters of the nanofluids

	Base fluid 1 (B1)			Nanofluid 1 (NF1)			Nanofluid 2 (NF2)		
Temp (°C)	*k*	*n*	R^2	*k*	*n*	R^2	*k*	*n*	R^2
25	3.92	0.412	0.9993	5.15	0.492	0.9915	5.92	0.681	0.9998

Further, the profiles strongly suggest that NF2 exhibits pseudoplastic behavior which belongs to non-Newtonian fluid category. The NF2 data fits the power law model, which is often followed by chemical EOR additives, as described in Table 2.

3.2 Effect of Concentrations

Fig. 3 presents the effect of varying concentrations (0.5 to 1.25 g) of CuO (nano), nanoclay and conventionally used PHPA. It can be observed that viscosity of the base polymer solution is significantly increased with increasing concentration of additives. However, the base fluid (NF2) with CuO has shown much enhancement in the viscosity comparing to the other base solution where nanoclay and PHPA were varied. Thus, NF2 consisting of nanoclay and nano-CuO is a more promising viscosifying additive compared to PHPA. However, the lower viscosity achieved in the base fluid prepared with the nanoclay solution was due to an increase in the surface active properties of the polymer solution i.e., PHPA which in turn decreases the compactness of the macromolecula chains, which further results in lower viscosity of NF1 compared to NF2.

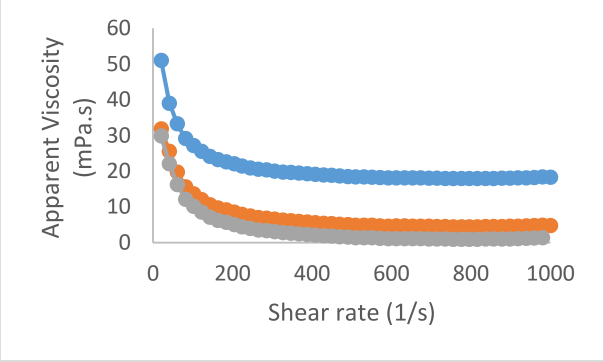

Fig. 2 – Apparent viscosity vs shear rate relation of the nanofluids

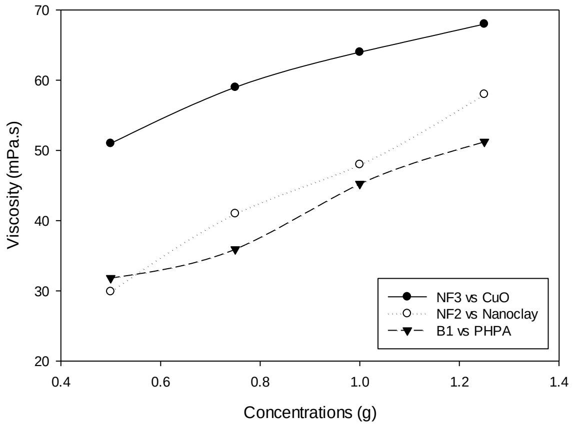

Fig. 3 – Effect of chemical additives on viscosity of the base fluids

3.3 Effect of KCl on the Viscosity

Fig. 4 shows the effect of salt contaminants on proposed polymer solution incorporation of CuO i.e., NF2, NF1 and B1 (PHPA polymer solution). It can be observed that NF2 is insensitive to the salinity. On the other hand, the viscosity of NF1 prepared with nanoclay and B1 formulated with conventionally used PHPA is observed to be reduce with increasing salt concentration. Such a decrease in viscosity was due to less dissolution of nanoclay in brine solution, which is generally prepared by mixing salt in water and breaking molecular chains of PHPA in NF1 and B1 at high salt concentration. Oil reservoirs are always associated with brine, so it is important to analyze the feasibility of any mobility control agent i.e., polymer as a displacing fluid prepared with brine solution. However, the presence of brine in the displacing fluid may also provide different reservoir data, which is important for evaluating dynamic properties like saturation present in the formation and types of fluid present inside the reservoir.

3.4 Effect of Temperature on the Viscosity

The effects of temperature on the nanofluid based polymer solution were investigated from 25 to 100 °C. The obtained results indicate that NF1 is not significantly affected by temperature compared to the conventionally used PHPA polymer system. In NF1, the viscosity has slightly enhanced with increasing temperature. This may be due either to the formation of new cross-linking sites during the chemical reaction or enhanced molecular mobility between the nanoclay and PHPA polymer due to the presence of copper oxide nanomaterial or coiling of copper oxide on the nanoclay and PHPA, which becomes the reason for the slight enhancement of viscosity at higher temperatures [18, 19].

The rheological constant for the power law model which fits the prepared polymer solution is described in Table 3. It is evident that with increasing temperature, the value of n increases for NF2, which is desirable for selecting the best candidate for mobility control assisted chemical EOR. However, a polymer solution having n ranging from 0.4-0.8 may provide better pseudoplastic property and also help in retaining viscosity after encountering different stain during the recovery operation. This phenomenon ensures the stability of displacing fluid under different situations in the reservoir at high temperature, which is another advantage when utilizing NF2 as a displacing fluid compared to commercially used polymers. Both B1 and NF1 are highly sensitive to temperature, since it is evident that the viscosity of both solutions decreases with increasing temperature, which is undesirable with EOR operation. However, the rheological constants also varied significantly, resulting in R^2 deviation for B1 and NF1, as seen from Table 3.

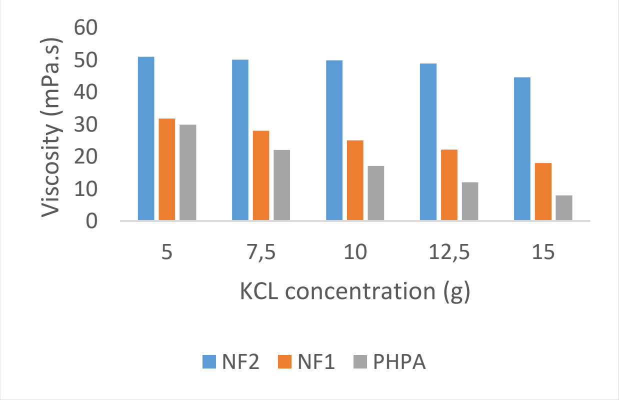

Fig. 4 – Effect of salt contaminants on the nanofluids

4. CONCLUSIONS

The nanofluid formulated from copper oxide (PHPA) has been investigated to improve the efficiency of oil recovery. Based on the rheological analysis, it can be concluded that the nanofluid prepared from copper oxide incorporating PHPA and nanoclay (NF2) exhibits pseudoplastic behavior with superior shear resistance with a reduction in its viscosity from 51-8.5 mPa.s. However, sensitivity analysis reveals that the viscosity can increase with increasing concentration of additives. The NF2 formulation is also insensitive to salinity and can withstand high temperatures.

Table 3 – Power law model parameters of the nanofluids at various temperatures

		Base fluid 1 (B1)			**Nanofluid 1 (NF1)**			**Nanofluid 2 (NF2)**		
Conc (g)	**Temp (°C)**	***k***	***n***	R^2	***k***	***n***	R^2	***k***	***n***	R^2
0.50	25	3.92	1.28	0.9223	5.15	1.16	0.9699	5.92	1.06	0.9783
	50	3.29	1.30	0.9212	4.53	1.17	0.9718	5.31	1.08	0.9802
	75	2.95	1.33	0.9025	4.19	1.20	0.9741	4.96	1.11	0.9825
	100	2.83	1.64	0.8762	4.06	1.52	0.9868	4.90	1.43	0.9952
0.75	25	5.29	1.26	0.9245	4.03	1.20	0.9670	7.29	1.04	0.9883
	50	3.88	1.14	0.9324	2.62	1.10	0.9749	5.88	0.93	0.9962
	75	3.02	1.09	0.9287	1.76	1.04	0.9712	5.02	0.88	0.9925
	100	2.92	1.03	0.8618	1.66	0.97	0.9834	4.92	0.81	0.9256
1.00	25	6.62	1.23	0.8893	4.97	1.09	0.9420	8.62	1.01	0.9789
	50	4.29	1.18	0.8956	2.64	1.03	0.9483	6.29	0.97	0.9852
	75	3.86	1.16	0.9020	2.21	1.00	0.9547	5.86	0.94	0.9916
	100	3.14	1.09	0.9086	1.49	0.95	0.9613	5.14	0.88	0.9982
1.25	25	6.88	1.26	0.9169	4.88	1.22	0.9783	8.88	1.04	0.9890
	50	5.62	1.20	0.9125	3.62	1.16	0.9739	7.62	0.98	0.9846
	75	4.14	1.19	0.8897	2.14	1.14	0.9612	6.14	0.97	0.9718
	100	4.04	1.17	0.9221	2.04	0.12	0.9836	6.04	0.96	0.9942

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Вплив наночастинок у технології підвищення вилучення нафти на основі полімерів

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Хімічні методи підвищення вилучення нафти на основі полімерів, хоч і усувають недоліки звичайного заводнення, такі як в'язке пальцеподібне нагрівання, мають проблеми з ефективністю в умовах соляного розчину та високих температур, які можна вирішити за рахунок застосування нанотехнологій. У роботі досліджується нанорідина, виготовлена з оксиду міді (PHPA), щоб підвищити ефективність вилучення нафти. Підготовлену нанорідину аналізують на її реологічні характеристики при різних концентраціях добавок, солоності та температурах від 25 до 100 °C. Аналіз передбачає, що нанорідина продемонструє значне покращення своїх реологічних властивостей із стійкістю до сольових та температурних умов.

Ключові слова: Підвищення нафтовіддачі, Хімічний, Полімер, Реологія, Нанотехнологія.