International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 18 (2018) pp. 13672-13676

Study the Rheological Behaviour and Effectiveness of Partially Hydrolyzed Polyacrylamide-Zirconium Acetate Gel System for Enhanced Oil Recovery

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Abstract

In this research article, a hydrogel was prepared on the purpose of performing a water shut-off process in an oil reservoir. The hydrogel was prepared by using the crosslinking of a partially-hydrolyzed polyacrylamide (PHPA) polymer and zirconium acetate. The tests were conducted to evaluate the effect of various parameters, such as temperature, polymer and crosslinker concentration on the gelation time using the bottle testing method. The effect of temperature on rheological parameters and hydrogel system was also studied. Phase diagram provides the optimum gel formation and effectiveness of optimum gel system was studied through the in-situ gelation and sand pack flooding experiments. The experiments show that the significant permeability reduction of the sand pack cores achieved at reservoir conditions by optimum gel system. Hence, this gel system may be suitable in water shut-off treatments required for enhanced oil recovery from the oil fields.

Keywords: Polymer gel, Gelation time, Water shut-off, Enhanced oil recovery

INTRODUCTION

Water production associated with crude oil production is one of the most common problems in matured oil fields. Worldwide, water production is around four times of oil production. Such excess water production decreases the well productivity, increases operating cost and profitability of oil and gas producing wells. Excessive water production also increased environmental problems and increased levels of corrosion and scales. The disposal of such amount of water needs high cost of water treatment facilities and water disposal systems. That high cost may leads to early shut-in of wells that still contain significant volumes of hydrocarbons [1-3]. For increasing the well productivity, the main focus on reducing this type of water production. By using different type of excess water control techniques, this type of water production can be controlled and reduce the affects generating by excess water production. Therefore, water shut off and conformance control represents a significant financial and environmental challenge for the petroleum industry [4-6].

There are several methods to control the excessive water production problems associated with enhanced oil recovery methods which include mechanical and chemical methods. The mechanical methods works on the mechanism of coning control via draw down reduction, co-production and down-hole separation, simultaneous water and oil production for coning mitigation and down-hole separation and disposal. But, the chemical methods are most suitable for reservoir related problems. Chemical means can be applied without a rig on location, making them more convenient for the operator and less expensive. Unlike cement and bridge plugs, chemicals including gelling polymers, can be placed deep into the formation. They form a gel that acts as a physical barrier that hinders the flow of water for a long period of time. The length of this period depends on the characteristics of the reservoir, the gel, and water movement in the treated reservoir [4, 7-8].

Among the mechanical and chemical methods, the polymer gel treatment is one of the most efficient methods to control excessive produce water production. Polymeric hydrogels, crosslinked with hydrophilic polymers, are the most effective methods to reduce the excess water production in the oil fields. Partially hydrolyzed polyacrylamide and chromium tri acetate based gel system most widely used for water shut-off in oil and gas wells. Depending on the polymer and crosslinkers composition, these gels are thermally stable, and the gel times are controllable over a wide temperature range. That gel system is injected to the reservoir which reduced the water permeability after proper gelation and consequently increasing the oil recovery. For the effective well treatment the two parameters (gelation time and the gel strength) are main parameters. Those two parameters strongly depend on the concentration of polymer and crosslinker and reservoir conditions such as temperature, hardness, salinity etc [7-9].

For pumping the polymer gel solutions into the formation, the rheological study is essential to know the flow ability before the placement of gel. The study of gelation time for any gel is very important because that will determine the injection period and how deep in to the formation the gel solution can be placed. The gelation time can be controlled by varying the polymer and crosslinker concentration and optimized for particular oil and gas well.

Various researchers studied the rheological and gelation behaviour of different gel system to provide the proper gel formulation. They also described different methods to obtain the properties of this gel system in laboratory and field applications. But, only few researchers did work on partially-hydrolyzed polyacrylamide (PHPA) polymer and zirconium acetate gel system [2, 3, 7]. However, these investigators did not perform rheological behavior, in-situ gelation and conduct sand pack flooding experiments for the effectiveness of the partially-hydrolyzed polyacrylamide (PHPA) polymer and zirconium acetate gel system. In this research work a partially-hydrolyzed polyacrylamide (PHPA) polymer and zirconium acetate gel system was prepared by cross-linking partially-hydrolyzed polyacrylamide (PHPA) polymer with and zirconium acetate crosslinker. The effects of different parameters, such as polymer concentration and crosslinker/polymer ratio, on gelation time were studied. Rheological analysis was also carried out to study the rheological behavior of the hydrogels to determine the flow behavior in well. Finally, the plugging ability of the polymer gel system was thoroughly investigated, by sand pack flooding at 90 ºC, to investigate their suitability for water shut-off jobs.

EXPERIMENTAL WORK

Materials and Methods

Partially-hydrolyzed polyacrylamide (PHPA) was obtained from Oil and Natural Gas Corporation Limited, Mumbai, India. Sodium chloride salt was procured from the Merck Pvt. Ltd., Mumbai, India and Zirconium acetate was purchased from Sigma-Aldrich, USA.

Preparation of the Partially-Hydrolyzed Polyacrylamide / Zirconium Acetate Gel

Firstly, partially-hydrolyzed polyacrylamide was dissolved in brine and constantly stirred on a magnetic stirrer until uniform to obtain a viscous solution. The viscous solution was aged at room temperature for 24 hours for the proper dissolution of the polymer in brine. A fresh solution of crosslinker was prepared in a different beaker and mixed with the viscous solution at a specific ratio. The pH of the gelant was maintained at room temperature using NaOH and HCl solutions. The gelant was taken in glass tubes and kept in a hot air oven at specific temperature and inspected visually for gel formation at regular intervals.

Characterization of Hydrogel System

The rheological properties, such as gelation time, gel strength and the gel deformability, were estimated by the bottle testing method. The gelation time for gel system can be determined by the two methods as bottle testing method and viscosity analysis method. Among the two methods, the bottle testing method is inexpensive, fast and semi-quantitative measurement method for the determination of gelation kinetics of different concentration formulations. For this purpose bottles with a capacity of 30 ml were filled with 15-20 ml of the gelant (mixture of cross-linker and copolymer). Bottles filled with gelant kept into the oven and investigated at frequent intervals by the tilting of bottles to observe gel formation. The gelation time was noted after gel formed and expressed in alphabetic code of A through J according to Syndansk's method as shown in table 1 [10,11]. The time of formation of gel strength of code C has usually been considered as a gelation time of water-shut off gels.

Table 1: Syndansk's code method and gel description

Code	Gel Description	Code	Gel Description
A	No detectable gel formed	F	High deformable non flowing gel
B	Highly flowing gel	G	Moderately deformable non flowing gel
C	Flowing gel	H	Slightly deformable non flowing gel
D	Moderately flowing gel	I	Rigid gel
E	Barely flowing gel	J	Ringing rigid gel

In addition, to represent the bottle test results in a more quantitative way, the viscosity analysis was conducted using a Physica Rheolab MC 1 (Anton-Paar GmbH., Stuttgart, Germany). In that experiment, 10 ml of each sample was taken and viscosity was measured at specific temperature.

Sand Pack Flooding Studies

Sand pack flooding studies were carried out to study the effectiveness of the optimized polymer gel system and compared with conventional hydrogel system (PHPA/Cr-Acetate gel) for water shut off purposes. In this study, a sand pack was prepared and Teledyne ISCO model 500D syringe pump was used for pumping the gel system into the sand pack core. The plugging capacity was determined using the same procedure as followed by several researchers working in this area [7, 8].

Calculation of Core Permeability: The linear Darcy equation was used to calculate the core permeability during this work. Sand pack permeability (k) was calculated using the following equation [12, 13]:

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

where Q is the flow rate, μ the viscosity of the brine, L the core length, Δp the pressure drop, and d the core diameter.

The plugging capacity of sandpack by gel system was calculated using the following equation [14, 15].

$$\eta\ (\%) = \frac{k_1 - k_2}{k_1} \text{X } 100 \quad (2)$$

where k_1 and k_2 are water permeability before and after polymer gel treatment, respectively.

RESULTS AND DISCUSSIONS

Phase diagram of Prepared Hydrogel System

In order to carry out gelation study, the bottle tests were conducted on different polymer concentrations (3000, 4000, 5000, 7000, 8000, 10000, 11000 ppm) with various

International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 18 (2018) pp. 13672-13676

crosslinker/polymer ratio (1/2, 1/3, 1/4, 1/5, 1/8, 1/10) at 90 ºC temperature and represented in phase diagram as shown in Figure 1. For the preparation of hydrogel system, the polymer concentration was critical to know the proper gelation which is called the critical overlap concentration. The different bottle tests results that the minimum concentration required for the preparation for hydrogel was 4000 ppm and below that concentration the proper gel was not formed. It was also shown that minimum polymer concentration and crosslinker/polymer ratio were 5000 ppm and 1/4 for the rigid gel formation. But the syneresis was happened as the polymer and crosslinker/polymer ratio became 8000 ppm and 1/3 respectively. The gel system showed syneresis phenomena because of the excess crosslinking. The phase diagram provides an optimum gel formulation by varying the polymer concentrations and crosslinker/polymer ratio and the optimum gel formulation was 5000 ppm of polymer concentration and 1/4 crosslinker/polymer ratio

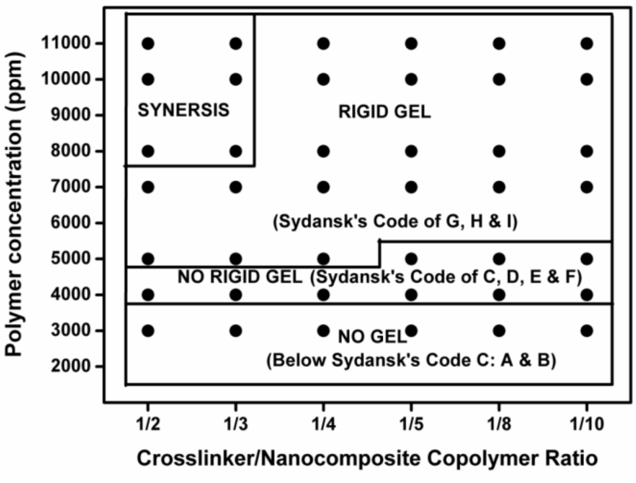

Figure 1: Phase diagram of the PHPA- Zirconium acetate hydrogel system

Effect of Polymer and Crosslinker Concentration on the Hydrogel System

The effects of polymer concentration and crosslinker/polymer ratio on the viscosity are shown in Figure 2 and Figure 3 respectively. For the study of polymer concentration effect on gel system, the samples were prepared with different polymer concentrations (5000, 7000, 8000, 10000 and 11000 ppm) and weight proportions of crosslinker/polymer 1:4 at 90 ºC temperature as shown in Figure 2. It was observed that the gel viscosity increased with the increase in polymer concentration. It was also observed that the polymer concentration affected the gel strength. From the results, it was shown that with increasing concentration of the polymer the gelation becomes more rigid as shown in Figure 1. For the study of crosslinker concentration effect on gel system, the samples were prepared with polymer concentration 5000 ppm and different crosslinker/polymer ratio (1/4, 1/8 and 1/10) at 90 ºC temperature as shown in Figure 3. It was observed that the gel viscosity increased with the increase in crosslinker/polymer ratio. It was also observed that the crosslinker/polymer ratio affected the gel strength. From the results, it was shown that with increasing concentration of the polymer the gelation becomes more rigid as shown in Figure 2. This may be due to more crosslinking sites and polymer bonds are available for the fast crosslinking reaction which increases the polymer concentration and increases crosslinker/polymer ratio.

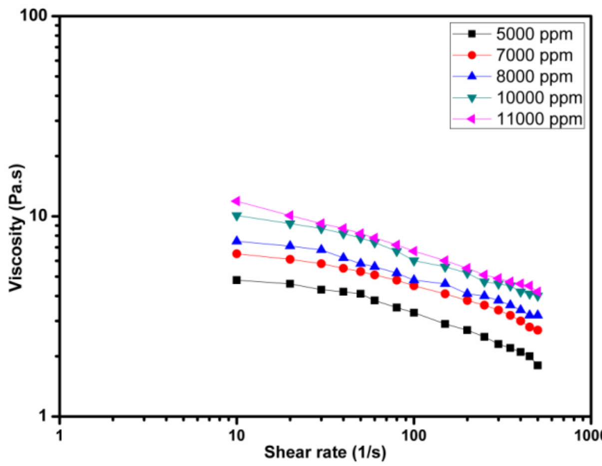

Figure 2: Effect of polymer concentration on gel viscosity (at 1/4 ratio of crosslinker/ polymer and 90 ºC)

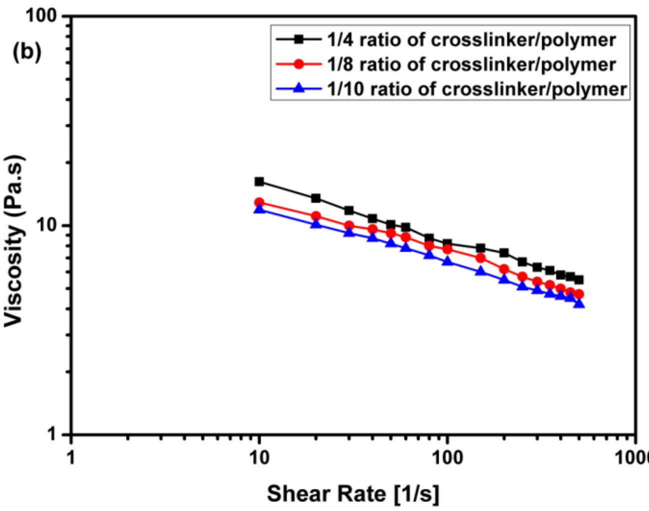

Figure 3: Effect of Crosslinker/polymer Ratio on gel viscosity (at 5000 ppm of polymer concentration and 90ºC)

Effect of Temperature on Gelation Time of Hydrogel System

The effect of temperature on gelation time and Arrhenius plot are shown in Figure 4 and Figure 5 respectively. For the study of temperature effect on hydrogel system, the samples were prepared with polymer concentrations 5000 ppm and weight proportions of crosslinker/polymer 1:4 at various temperatures (60, 70, 80, 90 and 100 ºC). The results show that the gelation time was decreased with an increase in temperature. This was due to either faster formation of new crosslinking sites during the chemical reactions or enhancement of the molecular mobility at higher temperature.

The gelation time is correlated to the temperature according to Arrhenius's equation [12]:

$$GT = M \exp^{E_a/RT} \quad (3)$$

Where GT is the gelation time in hours, M is the frequency factor (h), E_a is the activation energy (KJ/mol/K), R is the universal gas constant, and T is the gelation temperature (K).

According to equation 3, a plot of the natural logarithm for t versus 1/T should give a straight line with a slope of E_a/R and an intercept of lnM. Arrhenius relationship between gelation times at the above-mentioned temperatures for gels is shown in Figure 5. The activation energy of this gel system was measured to be 88.77 KJ/mol. The value of activation energy is relatively high for PHPA- Zirconium acetate hydrogel system which indicates that the reaction progresses not easily and reaction needs high energy to start the reaction. Therefore, this gel system can be used for deep wells.

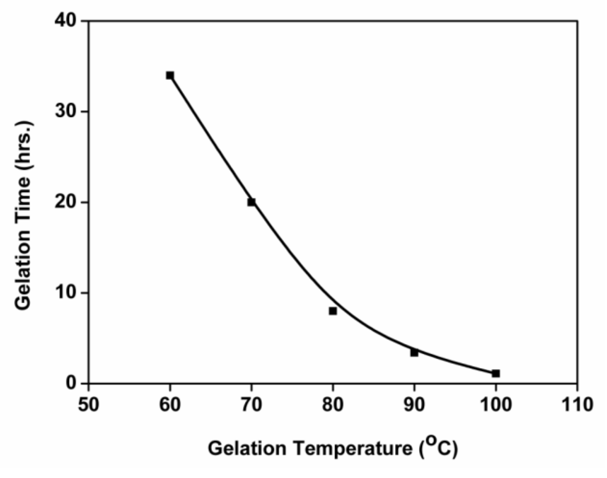

Figure 4: Effect of temperature on gelation time

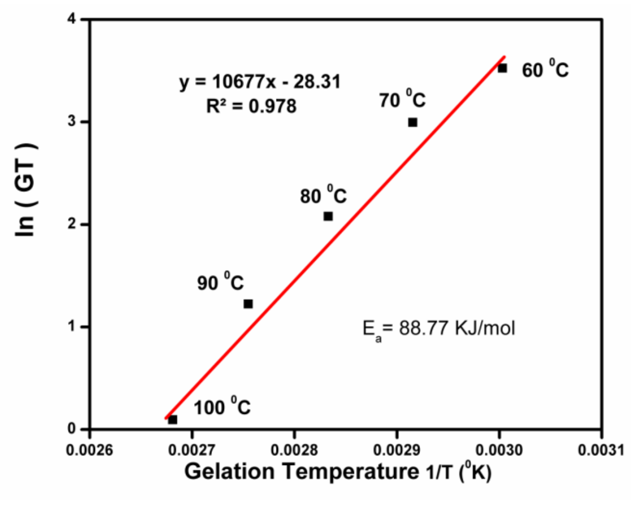

Figure 5: Arrhenius plot for PHPA- Zirconium acetate hydrogel system

Sand Pack Flooding Studies

The study of plugging capacity of PHPA- Zirconium acetate hydrogel and conventional gel (PHPA-Cr(III) acetate hydrogel) are shown in Table 2. For this study, sand pack flooding was used and compared with conventional gel system. From the experiment results, it was found that the porosity of the sand pack was 28.06% and initial permeability was 3.02 Darcy. Initially, the permeability of sandpack measured through water flooding than the PHPA- Zirconium acetate hydrogel and conventional gel system hydrogel solution was injected into the sand pack core. After that, sand pack with gel was kept in an air-oven for in-situ gelation at 90 ºC. After in-situ gelation, the brine was injected into the core to determine the plugging ability of the polymer gel system. By sand pack flooding experiment; it was observed that the plugging capacity of the core after the in-situ gelation of conventional hydrogel was 82.12%, whereas for the PHPA- Zirconium acetate hydrogel was 92.38%. The results show that PHPA- Zirconium acetate hydrogel was more effective than the conventional gel system. Hence, PHPA- Zirconium acetate hydrogel shows good plugging ability and suitability of this gel system for water shutoff job in the oilfields.

Table 2: Effect on gel system on the permeability of sand pack core

Sl. No.	Parameters	Observed Values	
		For PHPA- Zirconium acetate hydrogel	For PHPA- Cr(III) acetate hydrogel
1	Porosity	28.06%	28.06%
2	Initial Permeability	3.02 Darcy	3.02 Darcy
3	Post gelation permeability	0.23 Darcy	0.54 Darcy
4	Plugging Capacity	92.38%	82.12%

CONCLUSIONS

The bottle tests experiments results showed that the minimum concentration of polymer and crosslinker/polymer ratio were 5000 ppm and 1/4 to form the rigid gel system. The results also showed that the gelation time was decreased with the increase of polymer concentration and with the increase of cross-linker to polymer weight ratio and the gel syneresis was shown as the polymer concentration and crosslinker/polymer ratio exceeds 7000 ppm and 1/4 respectively due to the excessive crosslinking of polymer and crosslinker. The sand pack flooding results showed that PHPA- Zirconium acetate hydrogel system having sufficient plugging capacity, which shows its potential for water shutoff jobs in oil field for enhanced oil recovery.

ACKNOWLEDGMENT

The authors would like to gratefully acknowledge the DUIET, Dibrugarh University and IIT(ISM), Dhanbad for providing financial support and necessary laboratory facilities to carry out this work.

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