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Research Article

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An Experimental Analysis of Polyacrylamide Gel Polymer for Water Shutoff Operations

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Abstract As reservoirs become mature, huge quantity of water get to be produced alongside the hydrocarbon which results in a major production difficulty. Polymer gels have been tipped as a better option for shutting off water in reservoirs because they possess a good potential for reducing reservoir permeability to water, thereby making them effective in maximizing reservoir recovery. This study investigated a polymer gel solution formulated from the combination of polyacrylamide polymer, chromium acetate and thiourea. The chromium acetate and thiourea were the cross-linking agents. The formulated polymer gel was experimentally analyzed, and the effect of various parameters such as: salinity; polymer concentration; cross-linker concentration and pH on the gelation kinetics of the polymer gel were evaluated. The simulated reservoir temperature was maintained at 90^oC. The results showed that: an increase in salinity from 10,000ppm to 50,000ppm resulted in an increase in gelation time from 4.5 hours to 12.4 hours; an increase in the polymer concentration from 5,000ppm to 15,000ppm resulted in a decrease in gelation time from 21 hours to 8.2 hours; and an increase in the concentration of cross-linker from 1,000ppm to 5,000ppm resulted in a decrease in gelation time from 32 hours to 6.5 hours. Longest gelation time was observed at neutrality (pH of 7), but decreased as pH moved away from neutrality (acidic or basic). It was concluded that a right balance between the polymer and cross-linker concentrations was necessary in optimizing the polymer gel system.

Keywords Polymer, Water Shutoff, gelation, salinity, cross-linker

Introduction

In matured reservoirs, one of the significant production difficulties for the petroleum industry is the association of produced water with crude oil. Produced water is referred to as the water (brine) brought up from the hydrocarbon bearing formation strata during the oil/water separation process [1]. Increase in water production is usually prominent in aging reservoirs due to pressure decline or reservoir maturity. Even for new fields where there are cases of poor completion, poor reservoir management strategies and bad production practices, water breakthrough at early stages can be evident. Water oil ratio (WOR) is a very common term used in the petroleum industry in quantitatively describing the production of water. Equation 1.1 below defines WOR

$$WOR = \frac{Q_w}{Q_o} \quad (1)$$

Where Q_w is the water flow rate in barrels/day, and Q_o is the oil flow rate in barrels/day.

An average of 210 million barrels of water accompanied with 75 million barrels of oil is estimated to be produced daily which accounts for about three barrels of water per barrel of oil worldwide in the year 2000 [2]. This invariably means that WOR is globally on an average of 3:1. The amount of energy required to produce one barrel of water is equal to or sometimes more than the amount of energy required to produce the same volume of oil. Mohammed et al. in [3] stated that 81% of water was cut from some of the wells of Saudi Aramco in Saudi Arabia. Also, it was reported that 80% of water was cut from the wells of British Petroleum

(BP) and Kuwait Oil Company (KOC) in Sabiriyah field, Kuwait [4]. Produced water creates a huge problem in coordinating the logistics for disposing a large volume of water which could raise environmental and pollution concerns. Also, the cost of producing oil and gas is now very high as so many resources are committed to the handling of excess water that accompanies petroleum production, thereby drastically reducing profit. Operational problems such as fines production; sand production; increased rate of equipment corrosion; and increased tendency for emulsion and scale formation could be induced. Gel polymer treatment which could be seen as an IOR (Improved Oil Recovery) technique can be used to ensure a higher oil production rate and a lower water production rate provided all the necessary factors are being considered together with a proper selection method. For injection situations, the polymer gels are systematically positioned in layers in the reservoir producing the water. They are usually positioned in or around the near well bore region before cross-linking gets initiated. A gel which is a three-dimensional polymer structure is formed as the components of the polymer system react after its injection into the matrix of the target zone. A polymer that is soluble in water and a cross-linker are the usual components dissolved in water to form a polymer gel system. Polymer gel can be prepared and its physical and chemical properties tested against the various reservoir conditions including that of formation water using the bottle testing method. A good understanding of the polymer gel behaviour within the reservoir system can then be formulated. The gel formed can reduce or completely impede the flow of water through the porous media. Chemical treatment (a hydrophilic gel) could be used to seal off water channels that do not assist in the production of oil. When this gel is set, it must be well rigid so as to resist any kind of water passage through the water channels and the volume used for the treatment should be adequate in totally sealing off these channels [5, 6]. It may be very difficult to completely hinder the flow of water. In such situations, there are other chemical treatments that can be used to tactically reduce the permeability to water more than that to oil [5, 7]. The condition of the reservoir is a major determinant of the selection of a gel polymer system for a given well treatment. These reservoir conditions include; temperature, salinity, hardness and the pH of water used for the preparation of the gelant. There are other parameters to be considered for the proper selection of a given gel polymer system. They include salinity of the formation water, permeability of the target zone, and the formation lithology. Seikh and Mahto in [8] highlighted the negative effects of producing excess water and the benefits of adequately controlling excess production of water. They experimentally developed a polymer gel system using partially hydrolysed polyacrylamide polymer and inorganic (chromium acetate and thiourea) cross-linkers. They injected their developed polymer gel into Berea core samples and experimentally analyzed the effectiveness of the developed polymer gel in controlling excess water production. This they achieved by comparing the permeability gotten from this experiment under simulated reservoir conditions to the base permeability that was gotten from injecting only brine into the same core sample. They concluded that the developed polymer gel was effective in controlling water production from the reservoir as it reduced the permeability to water by 94.25% and that the higher the gel concentration the lower the gelation time. Sun and Bai in [9] carried out a comprehensive review of water shut off methods for horizontal wells. They highlighted the difference between the mechanical and chemical water shutoff methods. They carried out a case study analysis to determine the best water shutoff method for open hole completion, cased hole completion, and perforated liner completion. Open hole case study wells were cited and it showed the low success rate of mechanical packers in open hole completion method. The use of HEC polymer (chemical treatment) which was set by coiled tubing recorded significant successes. In one of the wells, the water cut reduced from 82% to 70%, while in another the water cut reduced from 60% to 40%. For cased hole, both the mechanical and chemical methods of water shutoff recorded significant successes. A polymer gel that comprised of HPAM and chromium acetate was used and it reduced the water cut from 90% to 72% and the oil production increased from 7.4 X $10^4 m^3$/day to 11.6 X $10^4 m^3$/day. A mechanical method which involved cement being squeezed into the reservoir using inflatable cement retainer (ICR) at a depth of 3073m also recorded a huge success. Water cut was substantially reduced while there was a huge increase in oil production. For perforated liner completion, a case study well for the mechanical method using cement rings showed a very good improvement. The water cut reduced from 80% to 5%. When chemical treatment was carried out, the water cut reduced from 80% to 50%. They concluded that mechanical methods are more expensive and that the correction depth is usually a big challenge. They further said that both the chemical and the mechanical methods can be utilized in open hole or cased hole completion in Horizontal wells while for slotted liner and sand screen completion, water shutoff can only be done by chemical treatment. Simjoo et al. in [10] carried out an experimental research on the use of polyacrylamide/chromium acetate polymer gel as a system for water shutoff operations in a reservoir in Iran. They carried out experiments to determine the effect of temperature, salinity and divalent cations on the gelation kinetics/gel strength of the polymer gel. From their experiment they observed the following: the composition of the gel and the environmental condition directly affects the gelation time; that a 5000 ppm polymer gel concentration, a 13,000,000 molecular weight and a 30% hydrolysis degree is the minimum needed for a 3-D gel network to be formed; as the weight percent of the polymer gel increases, the strength of the gel increases and the gelation time reduces; there is a limit to which an increase in the concentration of the cross-linker will enhance the gel strength; gelation time reduces as a result of the increase in the ionic strength by sodium and potassium salts; calcium and magnesium cations negatively affects the gel strength of the polymer gel, especially at higher temperatures; PHPA/Cr(III) gelation reaction is better done in alkaline pH. Polymer gel properties are significantly affected by temperature and other environmental factors; properties of polymer gel improves if environmental parameters are moderated from harsh conditions; and finally, unexpected plugging can be prevented by controlling the gelation time during injection and a proper adjustment of the environmental parameters. Baisali et al., in [11] experimentally developed an environmentally friendly polyacrylamide (PAM) polymer that was gelled together with an organic cross-linker (Hydroquinone/Hexamethylene tetramine) for water shutoff operations. They started by carrying out bottle test on the polymer sample to determine its gelation time and thermal stability. They observed how temperature, polymer concentration, salinity and cross-linker concentration affected the gelation time. They concluded that the polymer gel developed could greatly reduce permeability of the porous media to brine in high temperature reservoirs of about 120^{o}C.

The specific aim of this research work is to experimentally analyse the feasibility of Polyacrylamide polymer/chromium acetate/thiourea cross linkers for water shut off jobs in Niger Delta reservoirs.

Experimental Materials and Method

The following materials were used in carrying out this experiment: Polyacrylamide polymer powder; Chromium acetate; Thiourea; Sodium chloride; Calcium chloride; Hydrochloric acid; Sodium hydroxide; Sodium thiosulphate; Distilled water; pH Meter; Thermometer Density Bottle; U-tube viscometer; Liquid Permeameter; Weighing scale; Core samples; Beaker; Conical flask; Magnetic stirrer; Electrical heating system

The experimental methods here focus on the method used in analyzing the gelation time of the formulated polymer gel. This was done through the following process:

1. Room temperature distilled water was first used to prepare a predetermined quantity of the polyacrylamide gel so as to achieve the required gel concentration.
2. The polymer gelant solution was mixed with the cross-linker solution at various volume ratios (Polymer:crosslinker; 40:1, 20:1).
3. The pH of the mixture was then obtained using a pH meter.
4. The time it took for the mixture to form a rigid gel was recorded as the gelation time.

Salinity effects on the gelation time for the formulated gel

1. 10000ppm polymer gel (polyacrylamide) and 3000ppm of cross-linker (Chromiunm acetate and thiourea) were prepared by dissolving the required amount in various brine concentrations.
2. Steps number 2 to 4 from the experimental method section were repeated on the various mixtures to obtain the various gelation times.

Polymer concentration effects on the gelation time for the formulated gel

1. Various concentrations of the polymer gelant solution were separately mixed with the cross-linker solution.
2. Steps number 2 to 4 from experimental method section were repeated on the various mixtures to obtain the various gelation times.

Cross-linker concentration effects on the gelation time for the formulated gel

1. Various concentrations of the prepared cross-linker solutions were mixed respectively and separately with the 15000ppm prepared polymer gel.

2. Steps numbers 2 to 4 from the experimental method section were repeated on the various gel mixtures to obtain the gelation time.

pH Effects on the gelation time for the formulated gel

1. The prepared polymer gel solution was mixed with the prepared cross--linker solution at a ratio of 40:1 and stirred continuously until homogeneity was obtained.
2. The initial pH of the mixture was gotten and recorded with the aid of the pH meter.
3. The initial pH of the mixture was adjusted to 11, 9, 7, 5 and 3 by adding few drops of Hydrochloric acid and Sodium hydroxide as required on separated gel mixtures.
4. Step numbers 2 to 4 from the experimental method section were repeated on the various mixtures to obtain the gelation time.

Results and Discussion

It was reported in [10] that chromium acetate forms stable gel with polyacrylamide.

Salinity effects (concentration of salt) on gelation time

The pH, viscosity and temperature of brine were measured and recorded. The gel solution was aged at 90^{o}C using a microwave oven, while Figure 1 illustrates the relationship between the gelation time and the brine concentration.

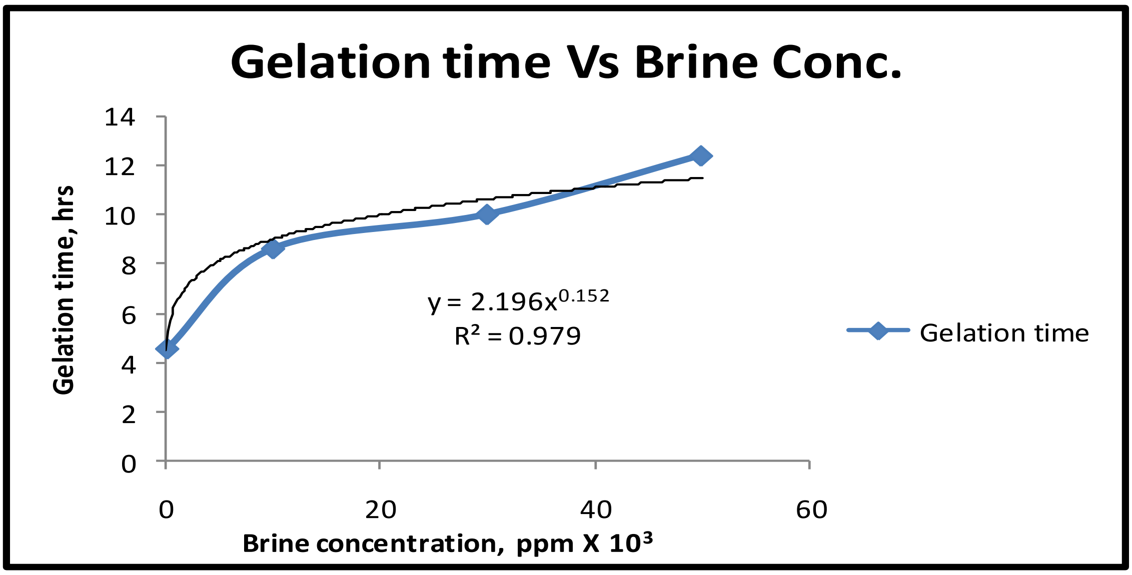

Figure 1: Effect of salinity on gelation time of 40:1 polyacrylamide/chromium acetate gel at 90 ^{o}C

From Figure 1, it was observed that increasing concentration of brine results in a corresponding increase in gelation time. A simple explanation for this trend had been reported by Tam and Tiu in [12]; Nasr-El-Din et al in [13]; and in [14]. The reason for the increase in gelation time from the addition of NaCl is the hydrolysis of the polyacrylamide polymer, which produces partially hydrolyzed polyacrlamide and ammonia under alkaline conditions. The partially hydrolyzed polyacrylamide which is being stretched by the negative charges produced from the caboxylate groups increases the polymer hydrodynamic volume. The positive ions that are being carried by sodium in NaCl screen the caboxylate groups and therefore make the partially hydrolyzed polyacrylamide coils to contract. The induction period is increased by this contraction, and therefore resulting in longer gelation times. As reported by Al-Muntasheri et al in [15], an increase in temperature results in an increased gelation rate and thereby reducing gelation time. From Figure 1 a power equation was developed, showing the effect of brine concentration on gelation time for polymer:crosslinker ratios of 40:1. This equation is shown in Equation 1.2

$$T_{gel} = 2.196 C_B^{0.152} \qquad (2)$$

Where T_{gel} is the gelling (gelation) time in hrs; C_B is the Brine concentration in ppm.

Polymer concentration effect on gelation time

The polymer concentration has a very strong effect on the characteristics and structure of the gel polymer network. According to Simjo et al in [10], the Critical Overlap Concentration (COC) value for polyacrylamide (synthetic polymer) is 5000ppm. The polymer-crosslinker ratio used was the 40:1. The gel solution was aged at 90^oC using a microwave oven. The results showing the polymer concentration effect on the polymer gelation time is displayed on Figure 2.

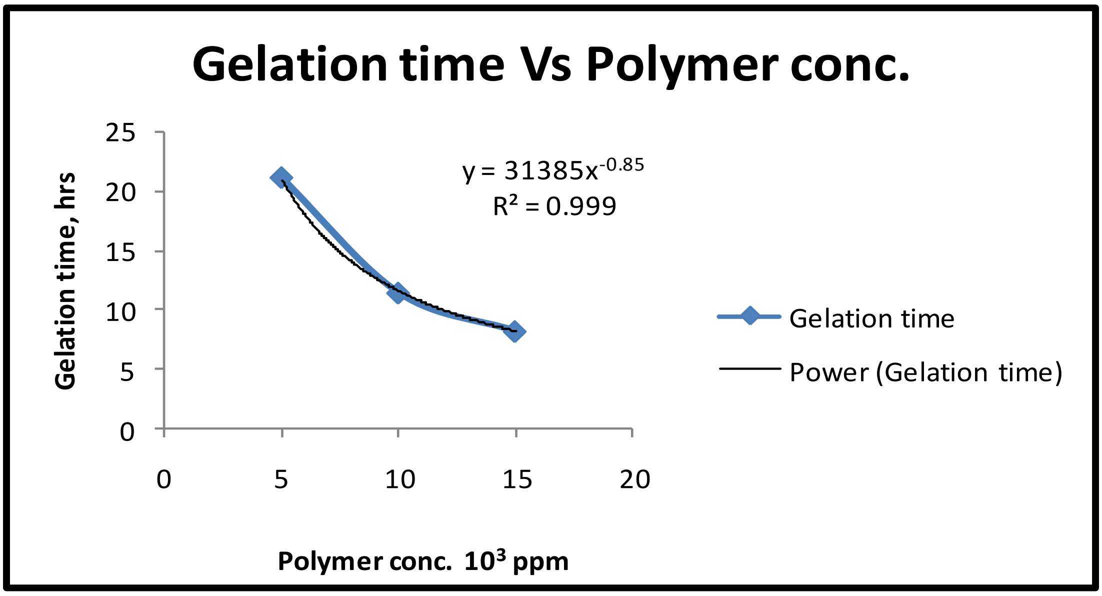

Figure 2: Polymer concentration effect on gelation time of 40:1 polyacrylamide/chromium acetate gel solution at 90^oC

The result shows that the gelation time reduced with increasing concentration of the polymer. Hence, raising the concentration of polymer will invariably shorten the gelation time of the gel especially in low temperature reservoirs. For high temperature reservoirs, delaying the gelling time could be easily achieved by decreasing polymer concentration. It is very important to note that, while using a low concentration polymer for high temperature reservoirs, we do not end up preparing very weak gels. Hence a good balance must be struck. When deep placements are anticipated, it is important we delay the gelation time by reducing the polymer concentration as well. A power law model was developed from the graphical relationship and it's shown in Equation 1.3 below.

$$T_{gel} = 31385 C_P^{-0.85} \quad (3)$$

Where T_{gel} is the gelation time in hours; C_p is the Polymer concentration in ppm

Cross-linker concentration effect on gelation time

A polymer gel formulated with only polyacrylamide might not result in the desired gel characteristics necessary in attaining stability. Hence, cross-linkers (cross-linking agents) are added to the polymer to obtain better physical gel properties that will adequately facilitate the plugging of porous media. The effect of chromium acetate/thiourea cross-linker on gelation time was examined by estimating the gelation times of the polymer gel using the following cross-linker concentrations: 1000ppm; 2000ppm; 3000ppm; 4000ppm and 5000ppm respectively. The volumetric ratio of the polymer-crosslinker gel solution was 40:1 for all cross-linker concentrations. The results showing the cross-linker concentration effect on the polymer gelation time is displayed on Figure 3.

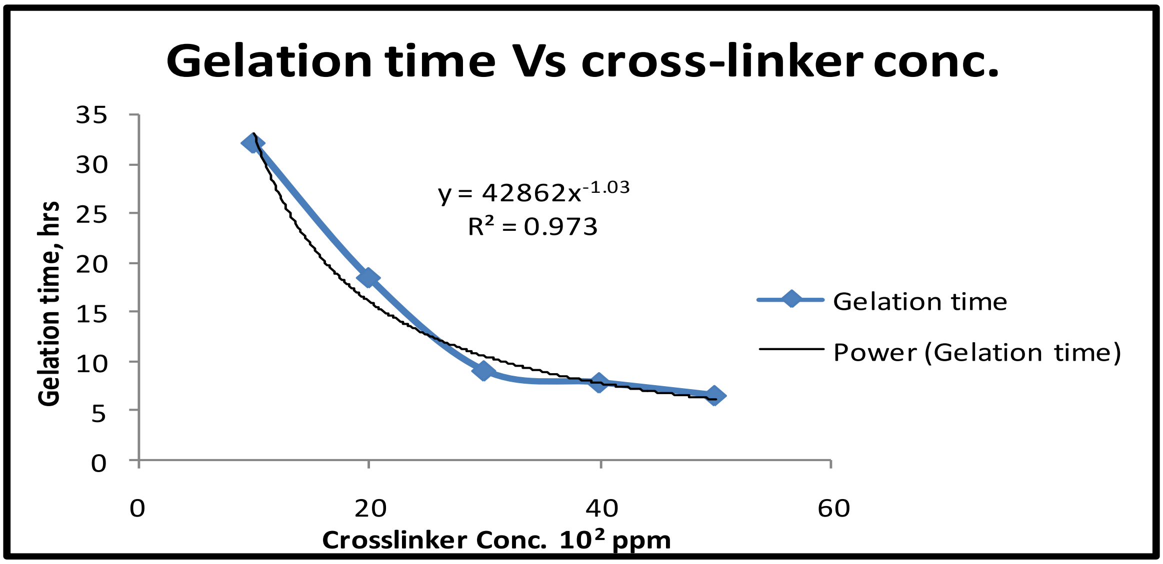

Figure 3: Cross-linker concentration effects on gelation time of 40:1 polyacrylamide/chromium acetate gel at 90°C

From the result it was observed that polymer gelling time reduced with increasing cross-linker concentration. From this observation, it could easily be said that by varying the concentration of the chromium acetate/thiourea, the gelling time could be easily adjusted. However, it was noted that at higher cross-linker concentrations, gel syneresis could occur. According to Bryant et al in [16], syneresis is undesirable especially when treating reservoirs with naturally occurring fractures. As shown on Figure 3, a mathematical model (power law model) was developed and it depicts the relationship between the cross-linker concentration and the gelation time. Equation 1.4 as seen below shows that relationship

$$T_{gel} = 42862 C_{cr}^{-1.03} \quad (4)$$

Where T_{gel} is the gelation time in hours; C_{cr} is the cross-linker concentration in ppm.

Effect of pH on the gelation time

Considering that ion exchange takes place in the reservoir, it is important to quantify the effect of pH in gelation time. As was stated in the method section, polymer gel of different pH values were prepared and monitored as a function of time. pH values were adjusted by adding Hcl to or NaOH as the case may be. The volumetric ratio of the polymer-crosslinker gel solution remained at 40:1 for all pH values. The summary of the results obtained for pH effect are shown below in Figure 4.

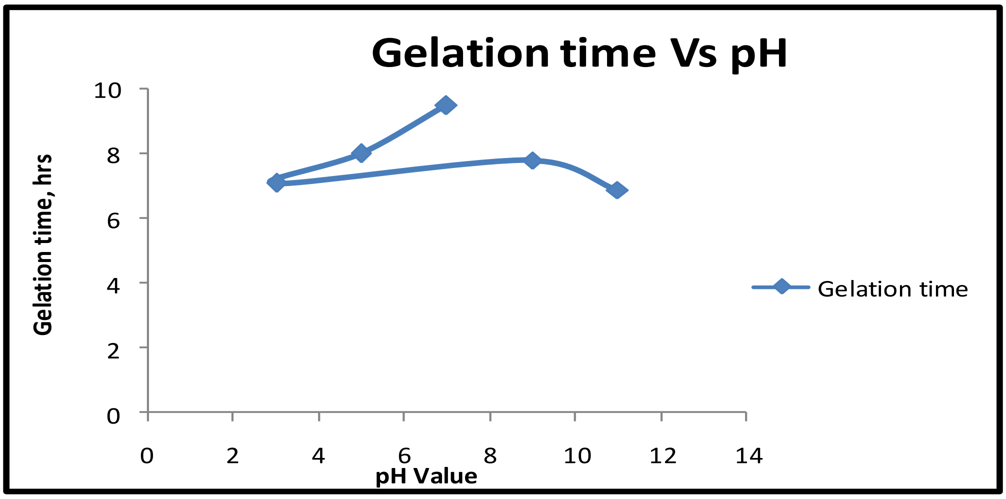

Figure 4: pH effects on gelation time of 40:1 polyacrylamide/chromium acetate gel at 90 °C

From Figure 4 it was observed that when pH was 7.0, we had the longest gelation time which eventually reduced as the pH moved away from neutrality (going acidic or basic). The variation in hydrolysis rate of amide groups present in polyacrylamide could be the cause of this. At the point when pH was 7.0, the hydrolysis was minimal which resulted in the longest gelation time of 9.5 hours. The hydrolysis rate increased as the pH drifted away from neutrality (going above or below 7.0). Therefore, from the results displayed we could see the gelation time reduced to 8.0 and 7.1 at pH values of 5.0 and 3.0 respectively. The same trend was observed for pH values 9.0 and 11.0, the gelation time reduced as well. Therefore, an increase in hydrolysis degree can effectively reduce the polymer gelling time. Since it has been observed that pH can affect gelation time, it is therefore important to take into cognisance any exchange of ions that could possibly occur between the reservoir and the gel solution.

Conclusion

In this research study, polyacrylamide polymer cross-linked with chromium acetate/thiourea was investigated. The basis of analysis of the polymer gel was on its tendency to form stable gel under simulated reservoir temperatures. Based on the experimental and mathematical analysis carried on the formulated polymer gel system, the following conclusions were drawn:

1. The gelation time of the polyacrylamide-chromium acetate/thiourea polymer gel system can always be controlled depending on the composition of the gel and the environmental conditions.
2. The Polyacrylamide gel is negatively affected by salt in the sense that the polymer gelation time increases with an increase in the concentration of salt. Salts can therefore be used as retarders for the polymer gel when high reservoir temperatures are anticipated.
3. The higher the polymer concentration the higher the rate of gelling. This means that a higher polymer concentration results in a reduced gelation time. Increasing the polymer concentration can therefore be used to accelerate gelation time.
4. Increasing the concentration of the chromium acetate/thiourea cross-linker promotes gelling. In order words, the gelation time decreases as the cross-linker concentration increases. The chromium acetate/thiourea cross-linker can be as an accelerator for gel formation.
5. The formulated polymer gel in this study has its longest gelation time when the pH is 7. In order words, gelation time increases as the polymer gel solution approaches neutrality. Acids and bases can be used to accelerate gelling of the polymer.

References

[1]. Scott W. (2007). United States Environmental Protection Agency's (USEPA's) Produced Water Permitting Requirement Report, Region 6. www.touchoilandgas.com/usepa-produced-water-permitting-a7136-1.html

[2]. Bailey, B., Crabtree, M., Elphick, J., Kuchuk, F., Romano, C. and Roodhart, L. (2000). Water Control. *Oilfield Review*, 12(1): 30-51.

[3]. Mohammed, M.A., Al-Mubarak, M.A., Al-Mulhim, A.K., Al-Mubarak, S.M. and Al-Safi, A.A. (1998). Overview of Field Results Using TTBP as Effective Water Shut-Off Treatment in Open-hole Well Completions in Saudi Arabia. *Presented at the 1998 SPE/DOE Symposium on Improved Oil Recovery, Tulsa, OK, 19-22 April, SPE 39616.*

[4]. Clark, R.A., Lantz, J., Karami, H. and Al-Ajmi, M. (2007). Pattern Balancing and Water flood Optimization of a Super Giant: Sabiriyah Field, North Kuwait, a Case Study. *Presented at the 2007 International Petroleum Technology Conference held in Dubai, UAE, 4-6 December, IPTC 11395.*

[5]. Sydansk, R.D. and Seright, R.S. (2007). When and Where Relative Permeability Modification Water-Shutoff Treatments Can Be Successfully Applied. *SPEPOJ*, 22(2): 236-247.

[6]. Sydansk, R.D., Xiong, Y., Al-Dhafeeri, A.M., Schrader, R.J. and Seright, R.S. (2005). Characterization of Partially Formed Polymer Gels for Application to Fractured Production Wells for Water-Shutoff Purposes. *SPEJ*, 20(3): 240-249.

[7]. Zaitoun, A. and Kohler, N. (1998). Two-Phase Flow Through Porous Media: Effect of an Adsorbed Polymer Layer. *Presented at the 1988 SPE Annual Technical Conference and Exhibition, Houston, TX, 2–5 October, SPE 18085.*

[8]. Seikh, M. and Mahto, V. (2013). Studies on Cross linked Polymer Gel System for Water Shut off Job. *International Journal of Engineering Research & Technology*, 2(10): 638-2641.

[9]. Sun, X. and Bai, B. (2017). Comprehensive Review of Water Shutoff Methods for Horizontal Wells. *Petroleum Exploration and Development*, 44(6): 1022-1029.

[10]. Simjoo, M., Valfaie, S.M., Dadvand, K.A. and Hasheminasab, R. (2007). Polyacrylamide Gel Polymer as Water Shut-off System: Preparation and Investigation of Physical and Chemical Properties in One of Iranian Oil Reservoir Conditions. *Iran J. Chem. Chem. Eng*., 26(4).

[11]. Baisali, S., Sharma, V.P. and Udayabhanu, G. (2011). Development and Performance of an Eco-friendly Cross-linked Polymer System for Water Shut-off Technique. *Presented at the International Petroleum Technology Conference held in Bangkok, Thailand, 7-9 February, IPTC 14381*.

[12]. Tam, K.C. and Tiu, C. (1989). Steady and Dynamic Shear Properties of Aqueous Polymer Solutions. *J. Rheology*, 33(2): 257-80.

[13]. Nasr-El-Din, H.A., Hawkins, B.F. and Green, K.A. (1991). Viscosity Behavior of Alkaline, Surfactant, Polyacrylamide Solutions Used for Enhanced Oil Recovery. *Presented at the 1991 SPE International Symposium on Oilfield Chemistry held in Anaheim, CA, 20-22 April, paper SPE 21028.*

[14]. Ghannam, M.T. (1999). Rheological Properties of Aqueous Polyacrylamide/NaCl Solutions. *J. Applied Polymer Science*, 72(14): 1905-1912.

[15]. Al-Muntasheri, G.A., Nasr-El-Din, H.A., Peters, J.A. and Zitha, P.L.J. (2005). Investigation of a High Temperature Organic Water Shut-off Gel: Reaction Mechanisms. *Presented at the SPE International Improved Oil Recovery Conference in Asia Pacific held in Kuala Lumpur, Malaysia, 5–6 December 2005, SPE 97530.*

[16]. Bryant, S.L, Rabaioli, M.R. and Lockhart, T.P. (1996). Influence of Syneresis on Permeability Reduction by Polymer Gels. *SPEPFJ*, 11(4): 09-215.