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Investigation of gel polymer as the water shut off in oil reservoirs

Milad Jadidoleslami[1]*, Ali Rahimi[2], Farshad Farahbod[3]

[1]Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Sirjan, (IRAN)

[2]Department of Petroleum Engineering, Science and Research Branch, Islamic Azad University, Fars, (IRAN)

[3]Department of Chemical Engineering, Firoozabad branch, Islamic Azad University, Firoozabad, Fars, (IRAN)

E-mail: milad.eslami2012@gmail.com; Rahimi_Ali_8681@yahoo.com; mf_fche@iauf.ac.ir

ABSTRACT

Today, the use of gel polymerto prevent water production in oil and gas wells is used extensively and many studies have been done in this field. The present study is an investigation of the gels, which are used in industry and in continuing the hydrolyzed polyacrylamide (PHPA) with cross-link of chromium acetate (III) was examined as the most used and cheapest gel polymer in the industry.

The effect of the hydrolyzed polyacrylamide (PHPA) concentration on the time and strength of gel is studied. The Increase of PHPA concentration andcross-link increase the gel strength thereby the gel time is reduced correspondingly. Moreover the impact of reservoir factors on the structure and the gel time is evaluated, temperature as the most influential factor of reservoir causes the gel being made faster with shorter times. In addition the impact of pH, pressure and salinity on the gel time is studied. The results show the use of PHPA with cross-link of chromium acetate (III) is an effective method in reducing water generation.

KEYWORDS

Water shut off;
Partially Hydrolyzed Polyacrylamide;
Cross-link;
Gel Polymer.

NTRODUCTION

One of the common problems in the development of theoilfieldis producing too much water,which unwanted water production is caused to reduce the effective permeability of oil thereby the efficiency of oil is decreased. Oil wells are facing with the increase of water production due to various reasons. One of the most common reasons of water generation is pressure drop of reservoir due to the production. As a result of this pressure drop, the contact surface of oil-water goes up and reached to the production well.

The limited capacity of theprocessing facilities, environmental problems, increase of the corrosion rate, sediment production are including of water production problems[2, 1]. Water production reduces the economic lifetime of the well[19]. There are different ways to prevent water production in oil wells, which are divided into two categories of mechanical methods and chemical methods. The mechanical method is like to close by cement or metal objects that is a sustained clamping and causes to closure the produced layer. Separation within the well and changes in the generative discharge or close the well for several days is horizontal drilling[4, 3], which is undergoing a huge cost[5]. Chemical methods unlike cementing methods and metallic objects don't closure the produced layer for permanentand it is a cheap and readily available method. The chemical method is the use of the gel polymer. Gel polymers are created based on a polymer and a soluble cross-link in water after passing sufficient time[6].

Gel polymers can be used to improve oil recovery. Actually the aim of the gelpolymer injection to the oil wells is decrease of relative permeability of water without any change in the oil permeability curve, although it may effect from water saturation on oil permeability[7, 3].

Selecting the appropriate gel polymer for preventing the production in oil wells is dependent on the reservoir conditions such as temperature, salinity, permeability and lithology. This gel polymer might be completely soluble in water to prevent the sediment in the empty spaces of thereservoir[8, 9].

Types of gel polymers

Gel polymersare madeby dissolving a polymer and a cross-link in water after required time. Generated gel should have high rheological property and also suitable strength, whichwould be resident in injection time and facing with stresses[12]. Polymers used in industry are divided into two categories:

a) Synthetic Polymer

b) Bio Polymer

Synthetic polymers are used for high temperature and acidity when they are mixed with the appropriate cross-link. The obtained gel from these polymers is relatively low cost because the major portions of the gel are being made by water. Polyacrylamide and copolymers can be noted among the synthetic polymers, which are used in industry. Biopolymers are insensitive toward divalent ions and have high thermal resistance to synthetic polymers. Being sensitive to microbial attacks is the disadvantage of using the biopolymers. Biopolymers are expensive and they are obtained difficulty to control the water production. Hgzantan and polysaccharides can be named as biopolymers[4, 10, 11, 24, 25].

Cross-link used in industry

As stated before the gel polymer is obtained by adding cross-link to the polymer solution. Cross-link causes the polymer chains are joined together and a three-dimensional structure of the gel occur and also the gel has more power and takes better rheological property[3]. The cross-link used in industry is divided into two categories:

a) Metallic

b) organic

Metal cross-link are such as boron, titanium, aluminum, zirconium, chromium(3), chromium(6), and the organic cross-links are such as phenyl acetate, hydroquinone, phenol, formaldehyde, hexamethylenetetramine which each of them is selected according to the conditions of reservoir and the used gel[3, 4, 5, 12].

Cross-link of chromium (3) and chromium (6) have been used widely. Usage of chromium (6) is not recommended due to it is sensitive to hydrogen sulfate and carcinogenic and toxic properties . Another reason for less use of chromium (6) is due to the difficulty of controlling the gel time. One way of solving this problem is adding reducer to the solution that converts the chromium (6) to chromium (3) thereby cross-link is reduced and, lets the gel solution to penetrate into deeper regions of the reservoir[20].

Chromium (3) is less toxic than chromium (6) and used widely. In addition, chromium (3) is used in high acidity conditions between 2 to 12.5 and it is insensitive to the carbon dioxide and hydrogen sulfate[15].

The use of aluminum is recommended more in accordance with its naturalness but it is used less due to it cannot control the cross-link.

Titanium and zirconium are less toxic toward chromium (3) and have less sensitivity to shear stress. Titanium and zirconium are used in the span of the well[21]. The organic cross-links are suitable for high temperatures. Cross-link links a covalent bond with the organic polymer and the reason of its sustainability at elevated temperatures is the covalent bonding. Moradi Araghi reported the stability of the organic cross-link to upper 120 °C. Cross-link of the formaldehyde and phenol is occurred between carboxyl groups in synthetic polymers and single cations but the main problem of phenol and

TABLE 1 : Examples of organic and metallic cross-link gelpolymer[26]

Polymer	Cross linker	Organic Or Metallic
PHPA	Aluminum citrate	Metallic
PHPA	Chromium acetate	Metallic
PHPA	Sodium dichromate	Metallic
PHPA	Zirconium lactate	Metallic
PHPA	Glyoxal	Organic
PAtBA	Chitosan	Organic
PAM	Hydroquinone/Hexamethyle- -netetramine(HQ/HMTA)	Organic
PAM-NaAMPS & PAM-VP	Phenyl acetate/HMTA	Organic
PAtBA	PEI	Organic

formaldehyde is toxicity and carcinogenic property[14]. TABLE 1 shows types of organic and metalliccross-links and their used polymer.

Selection of the gel polymer and appropriate cross-link

Selecting the appropriate gel polymer for preventing the water production in oil wells is the most important step in this operation. The gel polymer should be selected according to the environmental and repository conditions and it should have the consistency inside the reservoir. The hydrolyzed polyacrylamide (PHPA) with cross-link of chromium acetate (has demonstrated a better performance among all of the used gel polymers[9, 3]. Thereby investigation of the PHPA with chromium acetate is studied.

By dissolving a certain concentration of the PHPA in water and then adding a certain concentration of chromium acetate((toward PHPA to cross-link, usually 1:40 is more appropriate[3]) after a period of time a three-dimensional network gel polymer is produced.

The PHPA is made by adding a strong base such as sodium hydroxide to polyacrylamide at a certain temperature (about 60-80 °C) (Figure 1). The degree of hydrolyzed is a very important parameter and indicates the density of the polymer. The hydrolyzed degree is defined as the proportion of carboxyl groups divided to the total number of carboxylate and amide groups. If a polymer has the high degree of hydrolyzed it indicates a strong interaction between polymer chains and available cations in the solvent[11, 16]. ThePHPA is containing carboxyl groups and when the chromium acetate is added to thesplit, due to the weak bonding of ligand and chromium acetate, chromium is separated from its ligand and links with carboxylate group and controls the gel time[11, 4].

Effect of polymer concentration on the gel time

Polymer concentration for making the gel is critical and should always obtain the minimum polymer concentration for proper gel. There are different ways to measure the various properties of gel polymer; one of the used methods is the bottle test. This method is offered by Sydansk[18] and it is a cheap and fast method. The formation of the gel is determined by the codes between A to I. The code of A indicates non-formation of gel or it is the gel lubricant and thecode of I represents gel formation of three-dimensional. With study of conducted experiments it is identified that the increase of PHPA concentration decrease the gel time and increase the gel strength[12, 11, 8, 5, 4, 3, 1]. Polymer concentration should be adjusted in such a way thatthe gel would be formedat the time between 4 to 24 hours[17].

Effect of the cross-link concentration on the gel time

Cross-link gives better physical properties to the solution which close the porous media easier and protects the gel against destruction. Cross-link, causes the bond between the polymer chains and increase the molecular weight of solution and gives better rheological property to the gel. (Figure 2)

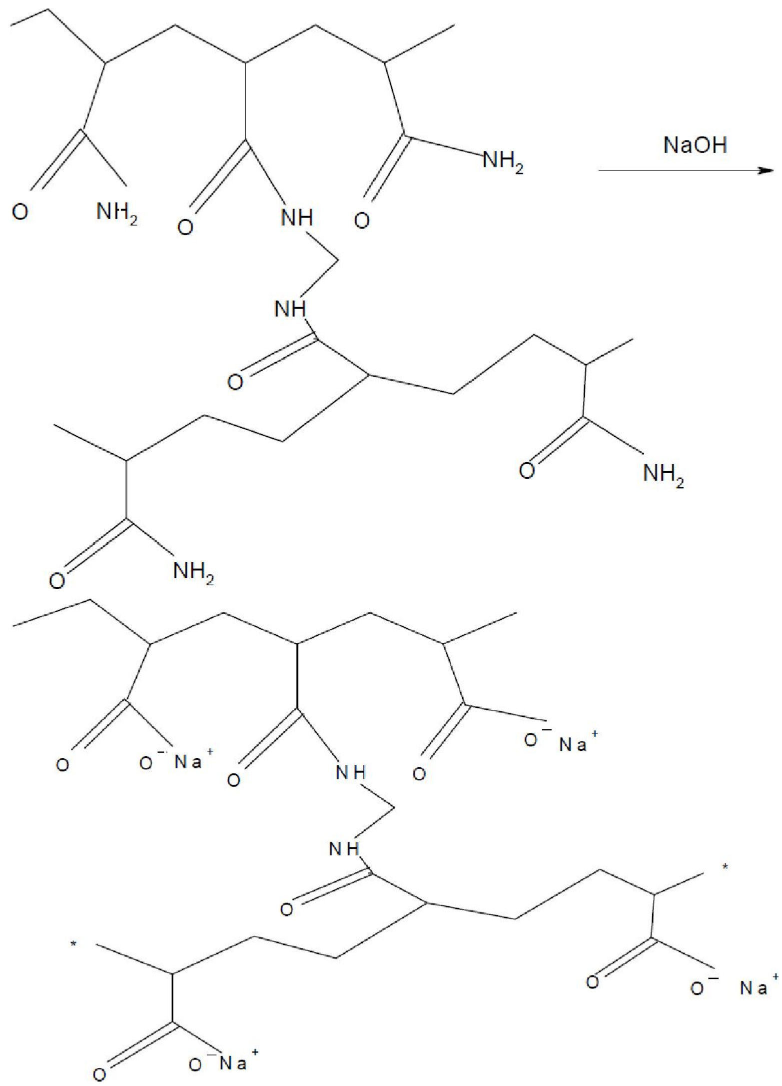

Figure 1 : Conversion of PHPA to polyacrylamide by a strong foundationsuch as sodium hydroxide at a temperature between 60-80 °C

Chromium acetate iscompletely solvent in water and by adding the cross-link to the solution; the lubricant gel is become non-rigid motion and makes a three-dimensional gel network occur. The speed of the gel increases with the increase of cross-link of chromium acetate and the gel time decreases thus the power and strength of the gel increase[4, 10]. Large increase of cross-link causing the polymer molecules get closer to each other and thenthe gel shrinks, which this causes the gel strength weaker thus the gel syneresis is occurred[3].

Effect of reservoir factors on the gel polymer

The influence of temperature

Temperature is a key factor to preventing the production of water and the gel time is affected severely. The increase in temperature increases the molecular mobility or the formation of new construction and the access of cross-link to the polymer is become longer thus the gelation made faster. The gel time depends on the temperature according to the Arrhenius equation 1:

$$GT = Mexp\left(\frac{E_a}{RT}\right) \quad (1)$$

GT: gelation time (hr); E_a: activation energy (kilo joules / mole / K); R: universal gas constant; T: temperature of the gelation according to the Kelvin; M: Frequency coefficientin terms of hour

According to the above equation, the gel time decreases with the increase of the temperature (Figure 3)[5, 18]. PHPA is affected by hydrolysisat higher

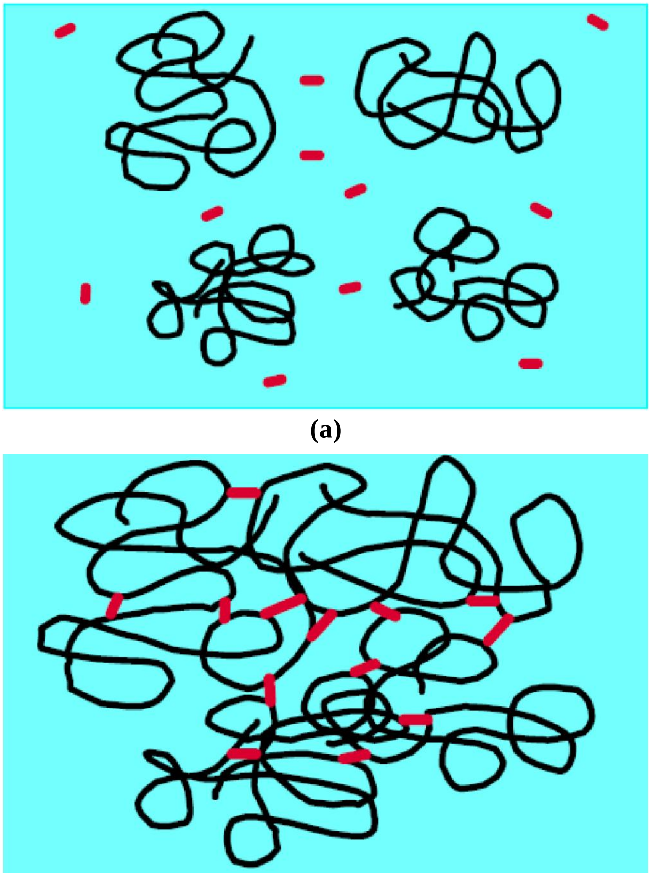

Figure 2 (a) : The polymer before cross-link reaction, (b) The polymer aftercross-link reaction[4]

gel strength is decreased.

Effect of the acidity

Gel polymers are formed in a wide range of acidity. It is formed in the acidity range of 4 to 10.5 and with increase of the acidity in this range the gel is formed faster, and the gel viscosity increases and in higher amounts of acidity of 10.5 due to additional generation of cross-link,the excessive reactions occur and causes a electrostatic amplitude in length of polymer chain, which increases the gel time but the gel strength decreases[11, 39]. In acidic system the gel viscosity increases initially, but after a periodof time it starts to decrease[5].

Effect of salinity on the gel polymer

One of the main influencing factors on the gel is the present of salts in the reservoir. With increase of the capacity of single ions of sodium and potassium,it is collected around the carboxyl groupdue to having the positively charged,which this causes the shrinkage of the polymer chain andcoils[11]. The presence of calcium and magnesium captions has a negative effect on the gel. Water that are containing calcium and magnesium caused a three-dimensional gel structure becomes precarious and reduce the strength of

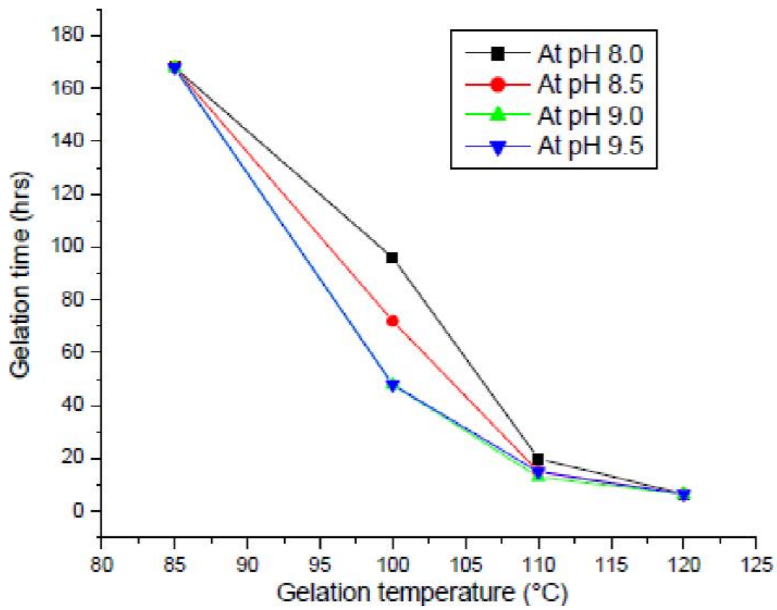

Figure 3 : The effect of temperature on the gel time at different acidity[23]

temperatures of 100 °C, the increase of hydrolysis causes the water gets out of the gel structure and the

the gel network due to the reaction between carboxyl groups with the negative charges of the polymer and divalent captions and even may cause the polymer to be deposited. The presence of divalent ions increases the gel time[5,22].

The effect of pressure on gel polymer

Pressure does not influence the gel strength. Sydansk has found the gel speed is a weak function of pressure and the speed of the gel might not change with the pressure. Pressure can be neglected in front of other parameters[8].

CONCLUSION

1 –The use of gel polymer is caused to close the way of water production while oil is produced from the same layer.

2 –The system of hydrolyzed polyacrylamide (PHPA)with cross-link of chromium acetate (is considered as an effective and cheap method compared to other known chemical methods to prevent water production.

3 - System of the PHPA with chromium acetate(in front of the reservoir factors, such as pressure, temperature and salinity showed less sensitivity toward other chemical methods.

4 - Gel time of the PHPA system with cross-link of chromium acetate(is decreased by temperatureand has little effect on the gel strength.

5 –The gel is formed in rangacidity between 4 and 10.5 but in the acidic environment its viscosity decreasesafter a while.

6 –The single valence ions decreases the gel time and the gel strength is also reduced.

REFERENCES

[1] M.Simjoo, Davand A.Koohi, Vafaei M.sefati, P.L.J.Zitha; May, Water shut off in a fracture system using arobust polymer gel, Paper SPE 122280 Presented at The SPE 1European Formation Damage Conference Held in Schereningen, Nether lands, 27-29 **(2009)**.

[2] D.D.Sparlin, Jr.R.W.Hagen; Controlling water in producing operations, Part1- Where it comes from and the problems it causes, World oil Journal, **(1984)**.

[3] M.Simjoo, Vafaei M.sefati, Davand A.Koohi, R.Hasheminasab; Polyacrylamide gel polymer as water shut off system: preparation and investigation of physical and chemical properties in one of the iranian oil reservoir condition, Iran.J.Chem & chem.Eng., **(2007)**.

[4] A.H.Kabir; Chemical water & gas shut off technology – an overview, Presented SPE Asia Pacific Improve Oil Recovery Kualalumpur Malaysia, **(2001)**.

[5] Al G.A.Muntasheri, Nasr-EL H.A.Din, I.A.Hussein; A rheological investigation of high temperature organic gel used for water shut off treatments, J.Pet, Sci.Eng., **59**, 73-83 **(2007)**.

[6] G.P.Karamakar, Chakraborty; Improved oil recovery using polymeric gelants: A Review., Indian.J.Chem.Tech., **(2006)**.

[7] A.Zaitoun, D.Rousseau, S.Nouyoux, P.Mallo, O.Broun; Using micro gels to shut off water in a gas storage well, Paper SPE 106042 Presented at The SPE interactional symposium on oil field chemistry held in houston, Texas, U.S.A., **(2007)**.

[8] R.Sydansk; Conformance improvement in a subterranean hydrocarbon – bearing formation using a polymer gel, US Patent, No 4683949, **(1987)**.

[9] D.D.Sparlin; Polyacrylamide can restrict water, Oil and gas production -it's your choice., Paper SPE 6473, Meeting on Operating Practices in Drilling and Production Of The SPE, Oklahoma, **(1977)**.

[10] B.Sengupta, V.P.Sharma, G.Udayabhanu; Gelation studies of an organically cross linked polyacrylamide water shut off gel system at different temperatures and PH, J.Pet.Sci.Eng, **81**,145-150 **(2012)**.

[11] R.Sydansk; A new conformance improvement treatment chromium (ÀÀÀ) SPE/DOE 17329, Presented at the SPE/DOE Enhanced Oil Recovery, Tulsa, Oklahoma, **(1988)**.

[12] Al G.A.Muntasheri, I.A.Hussein, Nasr-EL H.A.Din, M.B.Amin; Viscoelastic properties of a high temprature cross linked water shut off polymeric gel, J.Pet.Sci.Eng., **55**, 56-66 **(2007)**.

[13] K.Chan, T.Hughes, D.Borling, R.Sydansk; Pushing out oil with conformance control, Oil Field Review, **(1994)**.

[14] Moradi A.Araghi; A review of thermally stable gels for fluid diversion in petroleum production, J.Pet. Sci.Eng., **(2000)**.

[15] M.K.Abdo, H.S.Chong, C.H.Phelps, T.M.Klaric; Field experience with flood water diversion by complex bio polymer s, Paper SPE 12642 Presented at The 1984 SPE/DOE Fifth Symposium on Enhanced Oil Recovery, Tulsa, **(1984)**.

[16] M.E.Zeynali, A.Rabbii; Alkaline hydrolysis of polyacrylamide and study on polyacrylamide-co-sodium acrylate, Iranian Polymer Journal, **(2002)**.

[17] S.Mashhoor, Dr.Al-Anazi, H.Saleh, R.D.Al-Mutairi, H.Mohammed, Al-Khaldi, A.Ali, Al-Zahrani, S.Ibrahim, Al-Yami, Nihat, Gurmen.; June, Laboratory evaluation of organic water shut-off gelling system for carbonate formations authors, SPE-144082, presented SPE European Formation Damage Conference,, Noordwijk, Netherlands, 7-10 **(2011)**.

[18] D.S.Jordan, D.W.Green, R.E.Tery, G.P.Willhite; The effect of temperature on gelation time for polyacrylamide / Cr (ÀÀÀ) System, SPE.J, **22(4)**, 463-471 **(1982)**.

[19] T.Q.Ngyen, D.W.Green, G.P.Willhite, Mc C.S.Cool; Effect of gelant composition and pressure gradients of water and oil on disproportionate permeability reduction sand packs treated with polyacrylamide chromium acetate gels, paper SPE 89404, Presented at the SPE Symposium on Improved Oil Recovery, Tulsa, **(2004)**.

[20] R.J.Fulleylove, J.C.Morgan, D.G.Stevens, D.R.Thrasher; October, Water shut off in oil production wells-lessons from 12 treatment, Paper SPE 36211, Presented international Petroleum Exhibition and Conference, Abu Dhabi, 13-16 **(1996)**.

[21] P.D.Mofit, Moradi A.Araghi, V.R.Janway, G.R.Young; March, Development and field testing of a new low toxicity polymer crosslinking system, Paper SPE 35173, Presented Permain Basin Oil and Gas Recovery Conference, Midland, 27-29 **(1996)**.

[22] Moradi A.Araghi, P.Done; Hydrolysis and precipitation of Polyacrylamide in Hard Brines at elevated temperature, SPE REJ 2(21,189-198), **(1987)**.

[23] B.Senqupta, V.Sharma, Pand G.Udayanbhanu; Development and performance of an Eco-friendly crosslinked polymer system water shut off technique, Presented International Petroleum Technology Conference, Bangkok, Thailand, **(2011)**.

[24] S.L.Wellington; Bio polymer solution viscosity stabilization polymer degradation and anti oxidant use, SPE J, **23(6)**, 901-912 **(1990)**.

[25] A.Ghaithan, Al G.A.Muntasheri; Conformance control with polymer gels: what it takes to be Successful, Arab.J.Sci.Eng, **37**, 1131-1141 **(2012)**.

[26] J.K.Fink; Petroleum engineer's Guide to Oil Field Chemical and Fluid, 585-624 **(2012)**.