An Overview of the Performance of Eco-friendly Polymers for Improving Oil Recovery from Existing Oil Fields

Baisali Sengupta[1], V.P. Sharma[*], G. Udayabhanu[2]
[1]Petroleum Engineering Department, [2]Department of Applied Chemistry
Indian School of Mines, Dhanbad, India

ABSTRACT

The demand for fossil fuels especially crude oil as well as its price is increasing day by day and have led to the search for newer methods and techniques for oil extraction worldwide and these are collectively known as enhanced oil recovery methods. This paper reviews the present status of the different types of organic and inorganic cross-linked polymers used by the Oil Industry for increasing the oil production. The paper deals with the progress made in different fields of Enhanced Oil Recovery. The present study indicates the suitability, merits as well as disadvantages of a particular cross-linker with reference to the reservoir characteristics of different oil fields where the polymer can be successfully used.

Keywords: polymer gel, cross-linker, enhanced oil recovery, chemical flooding

[*]*Author for correspondence* E-mail: vps_ismpe@hotmail.com

INTRODUCTION

In order to meet the constantly increasing demand of energy especially of fossil fuels, new methods and techniques are being developed continuously for the extraction of crude oil. This has become even more essential in view of the poor recovery of oil, which is between 30–35% of the oil reserve. With the ever fluctuating price of crude oil in the world market with the trend being mostly upward, it has become imperative to improve the oil recovery rate by applying different techniques and processes that are used worldwide and are known as enhanced oil recovery (EOR) methods. Enhanced oil recovery is achieved by gas flooding, chemical flooding, thermal recovery, ultrasonic stimulation or microbial injection.

A brief description of the same is presented below:***Gas flooding***: It is presently the most-commonly used approach to enhance oil recovery. A gas is injected into the oil-bearing stratum under high pressure. This pressure pushes the oil up to the surface. In addition to the beneficial effect of the pressure, this method sometimes aids recovery by reducing the viscosity of the crude oil as the gas mixes with it. Gases commonly used for this purpose include carbon dioxide, natural gas or nitrogen. Carbon dioxide EOR is yielding excellent results. For example at present the US produces 245,000 barrels of oil per day by using this method [1].

Chemical flooding: There are several possible methods that have been practiced by oil industry. Some successful applications are injection of polymers such as polyacrylamide, xanthan gum etc which can either reduce the crude's viscosity or increase the viscosity of water which has also been injected to force the crude out of the stratum. Detergent–like

surfactants such as rhamnolipids are injected to lower the capillary pressure that impedes oil droplets from moving through a reservoir. Another method of chemical flooding is alkali caustic flooding which is used in such reservoirs which are susceptible to water flooding and have temperature less than $200°$F. Sodium silicate plays a major role as a multifunctional chemical in chemical flooding.

Thermal flooding: In this technique, either the oil is heated during its flow upward in the well bore, or in the pool, which would allow it to flow more easily towards the drill head. Other variants of this technology include hot water injection, continuous steam injection (also known as steam flooding), *insitu* combustion or cyclic steam injection. The main objective of all thermal methods is to reduce the viscosity of the in–place oil, which is accomplished by heating. A serious disadvantage of steam flooding is that a major part of heat supplied by injected steam is transferred to the reservoir rock.

Microbial injection: Microbial injection is a part of microbial enhanced oil recovery. This technique is not very much in use at present due to its higher cost but offers a lot of promise. Strains of microbes have been both discovered and developed (using gene mutation) which function either by partially digesting long hydrocarbon molecules, by generating biosurfactants, or by emitting carbon dioxide. The prime consideration of

this technique is the quantity of additional oil that can be produced from reservoirs by stimulating the growth of indigenous or injected bacteria. This is accomplished by adding nutrients to injection water.

Ultrasonic stimulation: Application of high-power ultrasonic vibrations from a piezoelectric vibration unit shakes the oil droplets from the rock matrices, allowing them to move more freely towards the drill head. This technique is most effective immediately around the drill head [2]. The first laboratory study regarding the influence of ultrasonic stimulation in enhancing oil recovery was carried out by Duhon [3] and applied practically in sandstone reservoirs.

Water production is a serious problem during oil production. Water production has to be controlled in order to reduce operating expenses such as pumping costs, oil/water separation costs, equipment costs, corrosion, scale and sand production treatment costs and environmental damage/liability. Moreover handling and disposal of produced water involves lot of investments as per regulatory laws of the land and to satisfy Enforcement agencies [4, 5].

Normally control of water production is carried out by adopting methods like cement/sand plugs, mechanical packers, sodium silica gels, resins, polymer gels etc. These methods are basically being used to stop

or reduce water cut and thus improving sweep efficiency, controlling conformance which will improve/increase the economic life of the reservoir. Mechanical plugging and cementing are the only options for high salinity and high temperature reservoirs; it is so due to the fact that their properties are independent of the presence of multivalent ions in water as well as the temperature of the reservoir.

As early as the beginning of twentieth century petroleum development companies were using beans and flax to exclude bottom water from oil wells in Kern River oil field. During 1920's oil industries started using a mixture of resin and coarse sand.

From the early 1920's through the mid 1950's cementing technology was used. A major part of this cementing information however, represented practices used after World War II. Cementing method was being used in about 2000 wells out of the total 3.5 million wells present worldwide before 1990 [6]. Initially hand mixing of cement was practiced for water shut off which was later replaced by the mechanical mixer or jet mixer. During 1920's only about 250 bags of cement and waste slurry was needed for each well which increased to 2500 bags of cement later on. No doubt cement has more strength than polymer gel and will resist high pressure gradients and is also acid resistant but cementing has follows two major limitations

1. cement slurry is made up of suspended solids, and thus it functions as cement bridges and cement slurries do not penetrate the formation or gravel pack.

2. there is always a danger that some productive sites may be permanently closed [7–10].

Resins have been used by the petroleum industry in view of the fact that unlike cement they provide liquid unlike properties and penetrate permeable formations and gravel packs and can halt fluid and gas migration among formations.

Resin is most successful when it is placed under static conditions. It can be considered as a good candidate when used in squeezing off pressured gas zones [11].

This paper aims to emphasize on the recent advances in the use of polymer/surfactant flooding and especially on ecofriendly polymers. This technique falls in the category of chemical flooding. Chemical EOR methods and techniques are advancement on conventional water flooding processes. The present study will also concentrate chronologically on the role of polymer gels dealing into water production problem. In order to undergo polymer flooding the production wells must have at least one of the following characteristics:

- high water oil ratio (WOR) (the economic limit of WOR is about 50:1).
- excessive unproductive water production.

- substantial movable oil saturation in the well pattern being treated.
- unexpectedly low oil recovery.
- early water or gas breakthrough.
- high fluid level in wellbore.

POLYMER GELS

By the middle of twentieth century, oil industry started using polymers such as polyacrylamides and polysaccharides for enhanced oil recovery. Polymers are macromolecules, made up of repeating units joined together. Molecular weight of the polymers ranges up to several million Daltons. The physical size of the polymer molecule can vary from sub micron to micron range. Polyacrylamides have been the most widely used polymers for water shut–off in production wells and for profile modification in injection wells; however, they can become unstable in high salinity water at high temperatures due to auto hydrolysis. These polymers can be cross-linked with transition metal ions, and the resulting gels are known to be more stable in harsh environments than the single uncross–linked polymer itself [6, 12, 13].

The polymer gels have certain advantages as compared to cement slug and they are:

1. the polymer is injected as a solution which penetrates the reservoir rock and reduces permeability in the near well bore area and at the perforations,

2. the solution can move up and down the outside of the well bore, sealing cracks and existing micro annuli within the original cement sheath, and

3. the gel left in the well can be cleaned out by jetting with either a mild acid solution or water whereas cement is much more difficult to remove as it sets.

Different polymer systems have been synthesized which are capable of sealing off the more permeable layers so that the flooding liquid could be diverted to the underswept, tighter regions of the reservoirs. The polymer gels increase the apparent viscosity of water which increases resistance to flow of water in the swept zones. Once the gels block these regions oil easily flows out [14, 15]. The polymers used for this purpose must have the following properties:

- should be thermally stable.
- should be stable enough to continue to impede flow for long periods at particular temperature, pH and salinity.
- should be miscible in water.
- should possess sufficient mechanical strength.
- should be ecofriendly.

A gel consists of a network of cross–linked polymers. Polymer solutions and cross-linking agents are mixed together in order to form a gelant solution. The gelant with time and chemical cross-linking develop a 3–D structure. This 3–D structure including

encapsulated water is referred to as gel. The gels prepared for enhancing oil recovery consists of about 0.5–3% cross-linked polymer which forms a three dimensional network holding about 99.5–97% water in an equilibrium state. In fractured reservoirs, a partially formed gel is injected. If any disturbance occurs in the equilibrium of gel due to changes in nature or extent of cross-linking then syneresis (expulsion of liquid from gel and consequent shrinkage in gel volume) takes place [16].

Characteristics of a Good Gelant

Some important characteristics of a good gelant are:

1. sufficient gelation delay so that the gel is formed after reaching the formation
2. proper injectivity
3. good propagation of gelant components
4. durability of the permeability reduction

Characteristics of Gelled Polymers

1. Gels are created when dry polymer is mixed in water and cross-linked with either a metal ion (usually chromium triacetate or aluminum citrate) or any organic compound.
2. Gelation time is controllable, ranging from a few hours to weeks; slower gelation time allows for more volume and deeper placement.
3. Gels have viscosity and elasticity ranging from slightly greater than fresh water to rubber like.
4. Gels can completely block the flow of fluid through all reservoir rock or they can preferentially reduce permeability and fluid flow through only the most permeable and conductive pathways.
5. Gels can be created with polymer concentration ranging from a few hundred to more than 50,000 ppm; low polymer concentration means less gel strength and higher concentration means more gel strength.
6. Gels are equally applicable to sandstone and carbonate reservoirs.
7. Gels are relatively inexpensive because they contain 98% or more water.

METALLIC CROSS-LINKERS

The metallic cross–linkers function through the formation of ionic bond between multivalent metal ions and the negative sites of a polymer such as partially hydrolyzed polyacrylamide or biopolymers.

Aluminium (III)

The gelation of polyacrylamide using aluminium citrate as cross-linking agent was first reported in 1974 [17, 18]. It has been applied in many fields with impressive economic success. The citrate ion protects the Al (III) from hydrolysis which could have otherwise produced the $Al(OH)_3$ making the metal ion unavailable for cross–linking with polymers. Gelation occurs best in fresh water

due to the fact that Ca^{2+} and Mg^{2+} present in saline water compete with Al^{3+} for citrate ions.

Advantages

1. This system of PAM/Al^{3+} is of low toxicity.

Disadvantages

1. Due to rapid rate of gelation, the depth of penetration into the formation will be limited.
2. The divalent ions (Ca^{2+}, Mg^{2+}) present in water can cause Aluminium/PAM to precipitate rather than gel.
3. This polymer system of PAM/Aluminium citrate is applicable only up to 85°C.
4. Gelation can be achieved only when brine slug is removed from the slugs of PAM and Aluminium citrate.
5. Al^{3+} cross-linked gels are more stable at low pH and low temperature.

Zirconium (IV)

Zirconium (IV) type gels are reported as being useful to achieve higher sweep efficiency [19] with following advantages and disadvatages.

Advantages

1. Non-toxic.
2. Interact strongly with carboxylate group to form complexes which are more stable than those formed by using Cr (III) or Al (III).

Thus, gels capable of withstanding high temperature than Chromium gels may be prepared by Zirconium cross-linking.

Disadvantages

1. These gels are difficult to be prepared.
2. Lumpy and heterogeneous gels may be formed by cross-linking Zr (IV) reagents with carboxylate containing polymers.

This problem of lumpy gel formation can be minimized by using small amounts of sulphate or carboxylate reaction moderators in the cross-linked composition which provides homogenous, strong and stable gels in a short time.

Titanium (IV)

Another gel system includes Titanium (IV)-Hydrolyzed Polyacrylamide.This gel can hold its strength at moderate temperature (50°C) for a long time thus making it suitable to be used in a moderate temperature oil reservoir [20].

Advantages

1. Relatively less expensive compared to Zirconium.
2. Adaptable to hard brine content, neutral pH conditions and moderate temperature oil reservoirs.

Disadvantages

1. Syneresis occurs at high temperature due to hydrolysis of the amide group.
2. Ti-HPAM is a weak metal ion cross-linked gel that is only suitable for application in a moderate temperature oil reservoir.

Colloidal Silica Gel System

Colloidal silica gel system refers to stable dispersions of discrete nonporous particles of amorphous silicon dioxide (SiO_2). This polymer gel got importance due to its non-toxic nature and minimal environmental risk. The proper concentration of colloidal silica required to get the best result is between 6–15 wt. %. It has relatively short gelation times. Greater the number of silica particles in solution lesser the gelation time. However due to lack of mechanical strength it can't be used for permeability reduction of fractures. Another major disadvantage is the high cost of the system and it's incapability for in depth permeability modifications. In this system gelation time is controlled by adjustment of pH and salinity. The advantage of this system is that it exhibits stability over a wide range of temperature [21].

Chromium (III)

Another polymer system includes Polyacrylamide cross-linked with either inorganically complexed or organically complexed Chromium (III). There are reservations regarding the use of Cr (IV) and Cr (VI) as these are carcinogenic whereas Cr (III) is safe and used as a cross-linker [22, 23].

Moreover inorganically complexed Cr (III) has control over gelation rate and can be used in brines containing significant hardness at temperature even up to 66°C. Organically complexed Cr (III) protects highly active Cr (III) by forming complexes

delaying gel formation.

The differences between organically and inorganically complexed Cr (III) are:

1. Reaction of organically complexed Cr (III) is relatively much slower at ambient temperature in the pH range 4–7 compared with the ligand exchange process between inorganic salts of Cr (III) and polymer under similar temperature and pH conditions. Thus, organically complexed Cr (III) have longer gelation time.

2. Organically complexed Cr (III) compounds seem to resist gel syneresis at high temperature.

Organically cross-linked Cr (III) is more effective and reliable in water shut-off treatments compared to inorganically cross-linked Cr (III).

Disadvantages

The problem with Cr (III) cross-linked PAM gels is that due to the nature of bonding between Cr (III) and the pendant carboxylate group, formation of insoluble chromium species can occur at high pH.

1. Thermal instability.

2. Unpredictable gelling times and gel instability in the presence of some potentially active chemical species.

The gelling times can be controlled by the addition of materials that chelate with chromium in competition with the polymer bound carboxylate group. One way to control

gelation time is introducing chromium ion as Cr^{6+} ion along with some reducing agent such as sodium thiosulphate to reduce Cr^{6+} to Cr^{3+} which results in slower rate of cross–linking reaction. Inspite of its disadvantages Cr (III) has been extensively used due to its high success rate and relatively low cost. Despite several reservoir related problems such as salinity, pH etc Cr (III) acetate cross–linked PAM compositions are reported to provide reliable performance in the field [24–27].

Limitations and Disadvantages of Metallic Cross-Linkers

1. Each metal has affinity for different functionalities. For example Al, Cr and Zr are reactive to amide and carboxyl groups while Titanium is reactive to hydroxyl group.

2. Proper pH control necessary for gelation.

3. Ligand metal bond formation and stability may be affected due to unfavorable conditions such as high ionic strength and the temperature of reservoir brine.

4. Unsuitable for high temperature applications [17].

5. A number of cross-linking agents are effective only under certain defined conditions of pH which may be different from alkaline conditions under which the polymers function most effectively.

6. Some highly charged metal ions such as Cr^{3+} have high charge density which tends to distort the polymer as a result of which the water may be squeezed out of the gel

structure so that it becomes less stable than desirable.

7. Certain metal cross–linking agents are relatively toxic and unfriendly to the environment, particularly due to the fact that the metal may enter aquifers from the oil bearing formations.

8. Some metal cross–linking agents such as Cr^{3+} are quite costly and it would be desirable to find cheaper alternatives.

9. They have low thermal stability.

10. Increased reactivity of metal cations is another key drawback.

11. Excess cross–linking occurs in some multivalent cations resulting in syneresis.

12. Have shorter gelation times.

The metallic cross–linker systems have several flaws and limitations in comparison to their advantages. Thus they are slowly being replaced by the more efficient organic cross–linker systems, which are being rapidly used in high temperature formations [28].

ORGANIC CROSS-LINKERS

The organic cross-linkers have slowly replaced the metallic cross-linkers, though organically complexed Chromium (III) is still yielding excellent results. These organic cross–linkers involve covalent bonding with the polymer molecule.

Advantages of Organic Cross-Linkers

1. Have high thermal stability. This stability is enhanced by the covalent cross-linking bonds.

2. Elastic modulus is higher for organic cross-linked gels.

3. Usually the nitrogen containing cross-linkers have a relatively lower charge density than many metal cations hence more stable gel structure is obtained.

4. Less sensitive to pH and lithology.

5. They are stable under a wide range of pH conditions hence are capable of effectively cross-linking a wide variety of polymers.

6. Less costly and toxic than many metal in formations connecting with aquifers and at lower cost.

7. Insensible to ionic forces, since they are formed through covalent bonding.

8. Organic gels are easy to implement and control during field operations due to flexibility in injection time [14, 29].

Amino Resins

Amino resins such as melamine/ formaldehyde are commonly used as organic cross-linkers due to few advantages.

1. Economically viable.

2. Applicable to a wide variety of polymers.

3. Form thermally stable, brine tolerant gels that are stable even at low pH.

4. No requirement of any acid or base catalyst [30].

Glyoxal

The polymer gel system consisting of Polyacrylamide and glyoxal is present as a sol always at low polymer concentration irrespective of the polymer concentration. With the increasing concentration of glyoxal the strength of gel increases. The gelation time of this system is strongly dependent on pH. Generally syneresis occurs at high concentration of glyoxal (>0.65g/l) [31].

Glutaraldehyde

Aldehydes such as glutaraldehyde have also gained attention when blended with polyvinyl alcohol. These gels are insensitive to the hardness level of water and can be used under harsh conditions such as high salinity, hardness and elevated temperatures. However these gels show excessive syneresis and gel shrinkage at high temperature [11].

Polyethyleneimine

Polyacrylamide-t–butyl acrylate/polyethyleneimine system is stable at high temperature. PEI cross–linker has low toxicity and was approved for food contact in the USA. PAtBA hydrolyzes to form partially hydrolyzed polyacrylamide and 3^0-butyl alcohol under conditions of low pH values and temperature and thermolyses at high temperature and pH values to produce partially hydrolyzed polyacrylamide and isobutene gas [32, 33]. PAM/PEI gels are stable up to a temperature of about 100°C. Polyethyleneimine as cross–linker is considered to be environmentally sensitive in some parts of the world, and therefore other alternatives were explored. This system is being replaced by less corrosive, less toxic,

less bioaccumulating and by systems which show better biodegradation [29].

Phenol/Formaldehyde

The Phenol/Formaldehyde system is used for high temperature applications. It is stable up to a temperature of about 150°C. These phenolic gels can be applied under harsh conditions such as high temperature, high salinity and high pH.It is also desirable due to its low viscosity and higher thermal stability. A major disadvantage of this system is that it is not ecofriendly [34, 35]. Gelation is somewhat sensitive to pH and salinity and hence was modified by sulphomethylating the phenolic compound. Another major drawback of this system is the loss of phenol through partitioning in crude oil [12].

A number of derivatives of Phenol and Formaldehyde have been used in order to reduce the toxicity of the polymer system. A polymer system consisting PAM cross–linked with Resorcinol/Formaldehyde, gels in shorter time at low temperature compared to Phenol/HCHO cross–linked PAM which gels in the same time at temperature greater than 80°C.The advantage of the Resorcinol /Formaldehyde system is the water like viscosity of the gelant which makes it desirable for gel treatment. Gelling is sensitive to pH of water and thus used in limited applications [4, 34].

Some recently used organic cross-linker systems instead of phenol/HCHO include combination of hydroquinone with hexamethylenetetramine, phenyl acetate/HMTA, resorcinol/HMTA etc. Formaldehyde is not ecofriendly thus researches till now have proved HMTA to be the only alternative for it. Some alternative cross–linkers with lower levels of toxicity producing stable gels have been suggested for phenol which includes o– and p-amino benzoic acid, m–aminophenol salicylic acid, phenyl salicylate etc. Among these, two systems i.e. HQ/HMTA and Phenyl acetate/HMTA have shown remarkable effectiveness due to their high mechanical strength and cost effectiveness. [36–40]

Aspirin/HCHO, Anthranilic acid /HCHO etc have also been used but have slower gelation rates and thus take longer gelation times compared to Phenol/HCHO at temperature of 70°C and above. The reason might be the slow rate of hydrolysis *insitu*.

Drawbacks of Organic Cross–Linkers

In spite of having several advantages the organic cross-linkers too suffer from certain drawbacks as mentioned below**:**

- must be stable not only at high temperature but also at high pH
- stability to various oil field brines
- systems at lower temperature require high cross–linker concentration

- syneresis is another major problem which if minimized would enhance the effectiveness of gels

- organic cross–linkers may be subject to partitioning in oil phase

HIGH TEMPERATURE GEL SYSTEMS

Nowadays selected higher temperature gel systems used include –

a. CC/AP (Chromium (III) carboxylate/acrylamide polymer) gels. These gels are chemically strong and form a relatively simple gel technology. They are inexpensive and can be applied either as gelants or as partially preformed gels.

b. Co–polymer of acrylamide and t–butyl acrylate cross–linked with Polyethylene – imine. This system has mainly two advantages due to which it gains attention-firstly, due to the fact that the PAtBA–PEI bonds are formed as a result of a nucleophilic attack by an amine nitrogen from the PEI on the carbonyl carbon of the polymer, this reaction does not require hydrolysis (or thermolysis) of the cross–linking site under reservoir conditions and secondly in PEI cross-linking, unlike many metallic cross- linkers, it is not susceptible to hydrolysis which helps it to propagate more efficiently through the reservoir.

c. Phenol/HCHO cross–linked acrylamide polymer gels including the possible use of less toxic derivatives of phenol and formaldehyde as the cross-linking agents. The derivatives that can be used include phenyl acetate, hydroquinone, resorcinol salicylic acid, phenyl salicylate etc in-situ. The only derivative that can be used instead of HCHO is HMTA [11, 41].

d. Lignosulfonate gels are simple, inexpensive and environmentally friendly. The characteristics of the gel formed are independent of the formation brine or carbon dioxide present. This system has high temperature tolerance and has long gelation times at high pH.

A new trend for gelation is being used in some oil reservoirs. It involves the application of gel as preformed particle gel (PPG). They are formed at surface prior to injection. This technique can overcome some distinct drawbacks inherent in in-situ gelation system such as lack of gelation time control, uncertainness of gelling due to shear degradation, change of gelant compositions etc. PPG has been successfully synthesized and applied to control excess water production. Studies carried out stated that preformed gel had better placement than in-situ gel and could effectively reduce gel damage on low permeability unswept oil zones. For their application the PPG particles are added to the injection water for some period of time, and then followed by normal water injection. Advantages of the PPG approach include that the product added has a known chemical composition, a PPG

suspension in the injection water created at the surface will have predictable physical properties, and these PPG suspensions can be stable and perform their desirable partial plugging action in the highest permeability zones of the reservoir at harsher reservoir conditions. The PPG technology, however, has two important limitations. First of all, these PPG particles swell almost immediately when exposed to water. Secondly, the PPG particles commercially available have a relatively large size (hundreds of microns to millimeters in diameter) which limits their application to plugging only very high permeability layers [42, 43].

Another promising agent for EOR application is micro gel. These micro gels are more tolerant to high temperature and salinities and more stable against degradation. These are used either as permeability modifiers or as viscosity enhancers. As the polymer micro–gel dispersion is injected into oil–bearing reservoirs the rheological properties and the flow property of the dispersions affect the profile control and the enhanced oil recovery significantly [44–46].

CONCLUSION

A lot of different polymer gel systems have synthesized till date but each of them suffer from certain limitations. It has been seen while reviewing the performance of different gel systems that they can be classified into two broad categories. There are some systems, which can withstand high temperature, and some, which have resistance to high salinity. Till date there is no such system that has the ability to stand both high temperature and high salinity.

Thus there is a wide scope of research and challenge to scientists involved in these areas to develop such cross–linked polymers, which can withstand both high temperature and high salinity.

ACKNOWLEDGEMENT

REFERENCES

1. Parker M. E. et al. *Energy Procedia* 2009. 1. 3p.

2. Xiaoyun T. et al *Transport in Porous Media Journal* 2007. 70. 323p.

3. Duhon R. D. *An investigation of the effect of ultrasonic energy on the flow of fluids in porous media* Ph.D. thesis, University of Oklahoma. 1964.

4. Vasquez J. et al. *SPE-93156* Paper presented at the SPE International

Symposium on Oilfield Chemistry held in The Woodlands, TX. February 2–4, 2005.

5. Davidson P. and Mentzer E. *SPE-9300* Paper presented at the 55th Annual Technical Conference and Exhibition, Dallas, TX. September 21–24, 1980.

6. Whitney D. D. et al. *SPE-30426* Paper presented at the SPE Offshore Europe Conference held in Aberdeen, Scotland. September. 5–8, 1995.

7. Xiaofen T. et al. *SPE- 88468* Paper presented at SPE Asia Pacific Oil and Gas Conference and Exhibition held at Perth, Australia. October 18–20, 2004.

8. Hoskin et al. *United States Patent No.4 785. 028* Mobil Oil Corporation, New York. 1988.

9. Seright R. S. et al. *SPE-70067* Paper presented at the SPE Permian Basin Oil and Gas Recovery Conference, Midland, TX. May 15-16, 2001.

10. Dalrymple D. et al. *SPE-28503* Paper presented at the SPE Annual Technical Conference, New Orleans, Louisiana. September 25–28, 1994.

11. Dovan H. T. et al. *SPE-37246* Paper presented at the SPE International Symposium on Oilfield Chemistry, Houston. February 18–21, 1997.

12. Al-Muntasheri G. A. et al. *Journal of Petroleum Science and Engineering* 2007. 55(1–2) 56p.

13. Needham R. B. et al. *SPE 4747* Paper presented at the 3rd SPE Symposium on Improved Oil Recovery, Tulsa. April 22–24, 1974.

14. Bryant S. L. et al. *SPE-36911 SPE Journal* December 1997. 447p.

15. Chang P. W. et al. *SPE-14235* Paper presented at 60th Annual SPE Technical Conference, Las Vegas, NV. 1985.

16. Kabir A. H. *SPE-72119* Paper presented at the SPE Asia Pacific Improved Oil Recovery Conference held in Kuala Lumpur, Malaysia. October 8–9, 2001.

17. Al-Muntasheri G. A. et al. *Journal of Petroleum Science and Engineering* 2007. 59. 73p.

18. Ranganathan R. et al. *SPE-52503* Paper first presented at the SPE International Symposium on Oilfield Chemistry, February 18–21, 1997.

19. Shu et al. *United States Patent No.4 676. 930* Mobil Oil Corporation, New York. 1987.

20. Wensheng C. and Ronghua H. *European Polymer Journal* 2001. 37.

21. Vossoughi S. *Journal of Petroleum Science and Engineering* 2000. 26. 199p.

22. Al-Muntasheri G. A. et al. *IPTC 11080* December 2007.

23. Lockhart T. P. *Society of Petroleum Engineering Advanced Technical Series* 1994. 2.

24. Lockhart T. P. *SPE-20998* Paper presented at the SPE International Symposium on Oilfield Chemistry held in Anaheim, CA. February 20–22, 1991.

25. Stavland A. and Nilsson S. *Journal of Petroleum Science and Engineering* 1995. 13. 247p.

26. Sydansk R. *SPE-17329* Paper presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Oklahoma. April 17-20, 1998.

27. Prada A. et al. *SPE-59322* Paper presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma. March 3-5, 2000.

28. Norton et al. *United States Patent No.4 561. 502* Marathon Oil Company, Ohio. 1985.

29. Al-Muntasheri G. A. *SPE-104071.* Paper presented at the First International Oil Conference and Exhibition held in Cancun, Mexico. 31 August – 2 September, 2006.

30. Mitchell *United States Patent No.4. 787. 451* Mobil Oil Corporation, New York. 1988.

31. Han M. et al. *Polymer Gels Network* 1997. 5(6). 471– 480p.

32. Albonico P. et al. *SPE-27609.* Paper presented at the European Production Operations Conference and Exhibition, Aberdeen, United Kingdom. March 15-17, 1994.

33. Al-Muntasheri G. A. et al. *SPE-105925* Paper presented at the SPE International Symposium on Oilfield Chemistry held in Houston, Texas, USA. 28 February–2 March, 2007.

34. Moradi-Araghi A. *SPE -27826* Paper presented at the SPE/DOE Ninth Symposium on Improved Oil Recovery, Tulsa, OK. April 17, 1994.

35. Reddy B. *SPE-75163* Paper presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma. April 13-17, 2002.

36. Bryant S. L. et al. *Journal of Petroleum Science and Engineering* 1997. 17. 197p.

37. Dovan et al. *United States Patent No.5. 617. 920* Union Oil Company of California, Calif. 1997.

38. Espenscheid et al. *United States Patent No.4. 613. 631* Mobil Oil Corporation, New York. 1986.

39. Hutchins R. D. and Dovan. H.T. *SPE-35444* Paper presented at the SPE/DOE. Symposium on Improved Oil Recovery, Tulsa, Oklahoma April 21–24, 1996.

40. Krilov Z. et al. *SPE-39676.* Paper presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma. April 19–22, 1998.

41. Moradi-Araghi A. *Journal of Petroleum Science and Engineering.* 2000. 26. 1p.

42. Yuzhang L. et al. *SPE-89389.* Paper presented at the 2004 SPE/DOE 14th Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, USA. April 17-21, 2004.

43. USPTO Application #: 20070204989. Fresh Patents.com. 2006.

44. Zhaoxia D. et al. *Petroleum Science.* 2009. 6. 294p.

45. Zweigle et al. *United States Patent No.4. 172. 066* The Dow Chemical Company, Midland, Mich. 1979.

46. Omari A. et al. *Journal of Colloid and Interface Science* 2006. 302(2). 537p.