Improved oil recovery using polymeric gelants: A review

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Oil and gas production from the reservoirs are often accompanied by huge amount of water production. Excessive water production from the oil and gas reservoirs is one of the major problems faced by the petroleum industries worldwide. Polymers and gels have been successfully used for many years to control the water production. Most methods involve cross-linked polyacrylamide gels initiated by metal ions or organic radical formation. Some inorganic compounds, particularly Fe(III) compounds can be transformed to gels by in-situ hydrolysis, which can be effectively used as the blocking materials. A new type of organically modified silicate compound, tetramethoxysilane (TMOS) has been supposed to be more effective in water shut-off jobs. In-situ cross-linking acid diverting agents (ISCADA) is proved to be a better solution to stimulate the multi-layered reservoirs. Certain biopolymers and foams may also be used successfully to control water production in oil or gas reservoirs. This paper attempts to review the present status of the gel systems used in the oil industries to control the water production during oil and gas production.

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The high water production during the production of crude oil from oil wells is a serious problem faced by the petroleum industries as it increases the production cost and creates water disposal problem. It also induces operational problems such as fines production, corrosion and scale formation. In the United States, where many fields are depleted, the ratio of water-to-oil production is closer to 9:1. In some areas around the world, fields remain on production when the ratio is as high as 50:1 (ref. 1). So to increase the oil recovery it is necessary to apply some effective methods for controlling the water production in wells. One of the solutions to reduce the production of unwanted water is the placement of full blocking gel systems in reservoir layers that produce the water. Most polymer gel systems available in the industry are placed in the near well bore before cross-linking takes place. After the injection of the polymer system in the matrix of a target zone, the components react and form a three-dimensional polymer structure. This three-dimensional structure is referred to as a gel. This gel can reduce or completely block water flows through the porous medium.

Another method involves injection of a suitable polymer solution into the production well, along with a cross linker, initiated by metal ions or organic radicals. The polymer solution and the cross linker then react to form an annulus of gel around the production well. This gel systems work as the relative permeability modifiers (RPM), modifying the flow of two phases, oil and water phases, and the phenomenon they induce is known as disproportionate permeability reduction (DPR).

TMOS/water system has a number of advantages over the conventional cement plugging. However, there is a scope of further research in this field, which involves the studies of rheological and thermal properties of the new type of gel system to be used in high temperature reservoirs and in harsh environment.

Polymers for water shut-off jobs/enhanced oil recovery

Polymer gels have been widely used to control the excess water production during oil and gas recovery. The use of polymers in Enhanced Oil Recovery is first suggested in the early 1960s as a means of reducing mobility ratio (M) by increasing the drive water viscosity and by reducing the formation permeability to water. The early pioneering work of Pye, Sandiford, Mungan et al. and Gogarty and later works of Smith and Szabo have shown that polymers at a very low concentration of a few hundred ppm can significantly increase the viscosity of the injected brine. Most of the early workers have worked with partially hydrolyzed polyacrylamide
(HPAM) gel. Sandvik and Maerker\(^9\) have worked with the biopolymer xanthan for field polymer flooding applications. Chang\(^10\) and others\(^11,12\) have evaluated field applications. Broseta \textit{et al.}\(^13\) have made some recommendations of the pertinent rheological measurements for an efficient gel screening in water shut-off and conformance improvement treatments. Hill\(^14\) claiming a patent has first proposed use of silicate gels in enhanced oil recovery. The idea of water shut-off treatments has been raised when injection of silicate solutions into oil producing wells with the aim at in-situ gelation to form a blocking phase is patented. Robertson and Oefelein\(^15\) are one of the few who have not only studied, but also tested the silicate gels for water shut-off applications. Later studies by Cole \textit{et al.}\(^16\) and Sparlin \textit{et al.}\(^17\) also have suggested that these materials can be successfully used for Improved Oil Recovery/Enhanced Oil Recovery purposes. Krumrine and Boyce\(^18\) have confirmed that the permeability modification with silicate gel based system is a viable alternative in need. Vinot \textit{et al.}\(^19\) have suggested the possible reasons of not using the silicate gels widely in practice; they have also pointed out the mechanism of silicate gelation under various reservoir conditions. Earlier studies\(^20\) with crosslinked polyacrylamide gels have been shown that the permeability of such a gel to water varies as power law function of fluid velocity. Al Sharji \textit{et al.}\(^21\) have shown that the permeability of water through the gel depends also upon the elastic properties of the gel. Recently, Grattoni \textit{et al.}\(^22\) have shown that TMOS is an effective oil soluble gelant which can be used as a RPM to control water production during oil recovery. Karkamar \textit{et al.}\(^23\) have shown that the gelation time and the RPM characteristics are function of the TMOS concentration. Hanssen \textit{et al.}\(^24\) report new experimental data for gas-blocking foams that appear to have superior oil tolerance caused by the presence of polymer. Lakatos and Kosztin\(^25\) have explained the laboratory studies and field results of disproportionate permeability modification by alcohol containing polymer solutions. A pilot test on the Hungarian gas fields has showed satisfactory results by using the alcoholic polymer solutions. Studies by Chauveteau \textit{et al.}\(^26\) describe in-depth permeability control by adsorption of micro-gels and the process to improve their field characteristics. Recent studies by Halder \textit{et al.}\(^27\) provide a new solution to stimulate multi-layered reservoirs by using \textit{in-situ} cross-linking acid diverting agent (ISCADA).

**Polymer gel systems used for water shut-off jobs**

Apart from mechanical tools, and the traditional cement and inorganic gel squeezers frequently used to isolate water out zones, several types of gelant systems have been used with some degree of success to control water production. There are three main types of chemical gel type treatments:

a) Permeability blockers or gelants\(^28\)

b) Disproportionate permeability reducers (DPR) and or Selective Permeability Blockers (SPB)

c) Relative Permeability Modifiers (RPM)

The two most commonly used polymers in such applications are partially hydrolyzed polyacrylamide (HPAM) and the biopolymer, xanthan. Recently, organically modified silicate compounds have been found to be effective in water shut-off jobs during oil production.

**Relative permeability modifiers in water shut-off jobs/Improved oil recovery**

**Polyacrylamide gels**

Polyacrylamide gels have been used to reduce water cut in production wells and control profiles in injectors. Formations up to 66°C have been treated rather routinely. Recently these gels are used at higher temperature formations containing relatively hard brines. A number of studies have been done with these gels cross-linked with trivalent chromium and aluminium with C-13 NMR\(^20\). These cross-linking ions react with the occasional carboxylate groups distributed along the polymer chain of polyacrylamides. When the metal ion-carboxylate reaction occurs the polymer chains are connected together in a three-dimensional network extending throughout the aqueous phase.

Dynamic rheological studies\(^30\) have been carried out with the cross-linked polyacrylamide gel by varying the gel strength while keeping the temperature, salinity and cross-linker concentration constant. Both the loss and storage moduli increased with the increase in polymer concentration of this gel system. Two parameters have been used to characterize the flow behaviour, one is intrinsic gel permeability and other is elasticity index.

The velocity-dependent behaviour of the gel’s permeability to water is due to its elasticity. Its intrinsic permeability is controlled by the distribution of dense and dilute domains with in the gel structure, while movement and deformation of the free polymer
molecules existing within the dilute domains govern its velocity-dependent behaviour.

Albonico et al. have reported that polymers or gels can effectively reduce permeability to water more than that of oil. Various types of gels that are studied included resorcinol-formaldehyde, Cr\(^{3+}\) (acetate)-polyacrylamide and Cr\(^{3+}\) (chloride)-xanthan and colloidal silica.

Later studies reveal a new and simple chemical approach to control the gelation reaction of Cr\(^{3+}\)/polymer solutions that substantially meets the gelation delay requirements for in-depth treatments of high-temperature reservoirs. By screening organic ligands for their gelation delaying power with hydrated Cr\(^{3+}\)/polymer and Cr(OAc)\(_3\)/polymer solutions several powerful retarding ligands have been identified. Use of the pre-formed Cr\(^{3+}\) complexes of these ligands together with additional, uncomplexed ligand in the gelant solution provide outstanding control over the gelation time over the temperature range of 60-135\(^\circ\)C. With these compositions gelation times spanning the range from several hours to one month or more have been obtained at temperature up to 120\(^\circ\)C. Due to low toxicity of the Cr\(^{3+}\) polymer gels the environmental problems are notably reduced relative to those employing hexavalent chromium compounds or formaldehyde.

**Inorganic gel systems in water shut-off jobs**

Certain Fe (III) compounds can be transformed into gel-like precipitate by in-situ hydrolysis, which is then immobilized by in-situ flocculation or spontaneous aging. Practical applications of Fe(III) compounds are restricted due to hydrolysis of such compounds in formation water. The iron-hydroxide formed in porous media becomes immobile due to spontaneous aging. However, its blocking efficiency is not much affected by temperature as iron-hydroxide is thermostable up to 150\(^\circ\)C. Besides Fe(III), Al(III) and Cr(III) theoretically fulfill the chemical requirements for such gel formation. The blocking materials have excellent stability under field conditions, but in case of technological failure the gel phase can easily be broken up into mobile sols. Internally activated sodium silicates (IAS) make up one of the most well established types of chemical sealants. The gelation times of IAS are controlled by the pH and temperature of the systems. The gelants form stiff, brittle solids at higher temperature with the use of same amount of silicates and high temperature activator (HTA). Silicate gels are generally stable above 200\(^\circ\)C, irrespective of the type of activator used.

**Oil soluble silicate gels in water shut-off jobs**

Besides polyacrylamide gels and inorganic silicates, organic silicates have been also used widely in water-shut-off applications. These gels usually provide some better results than the others in high temperature reservoirs.

The main advantages and disadvantages of using silicate gels in enhanced oil recovery can be summarized as follows:

**Advantages**

(i) Flexibility in chemical mechanism
(ii) Chemically and thermally stable
(iii) Easy gel breaking in case of technical failures
(iv) Simple and cost effective surface technology
(v) The silicates are environmental friendly materials

**Disadvantages**

(i) Rigidity of the gel leads to its fracture
(ii) Gelation kinetics is difficult to control
(iii) Penetration of the treating solutions is short if the buffer capacity of rock is high

**Organically modified silicate compounds for water shut off jobs**

Recently some research has revealed that organically modified silicate compounds such as tetramethyloethosilicate (TMOS, also known as tetramethoxysilane) can be used as relative permeability modifiers in water shut-off jobs which form an oil soluble gelant in wells during oil recovery. This alkoxide can be hydrolyzed and condensed under relatively wide range of conditions to form a rigid, porous gel as shown by the schemes 1, 2 and 3.

(i) Hydrolysis

\[
\text{Si-(OCH}_3\text{)}_4+n\text{H}_2\text{O} = \text{Si-(OCH}_3\text{)}_4-n\text{(OH)}_n+n(\text{CH}_3\text{OH})
\]

…(1)

(ii) Condensation

\[
(\text{OCH}_3\text{)}_3\text{-Si-OH}+\text{HO-Si-(OCH}_3\text{)}_3
\]

= 

\[
(\text{OCH}_3\text{)}_3\text{-Si-O-Si-(OCH}_3\text{)}_3+\text{H}_2\text{O}
\]

…(2)

and/or

\[
(\text{OCH}_3\text{)}_3\text{-Si-OCH}_3+\text{HO-Si-(OCH}_3\text{)}_3
\]

= 

\[
(\text{OCH}_3\text{)}_3\text{-Si-O-Si-(OCH}_3\text{)}_3+\text{CH}_3\text{OH}
\]

…(3)

The gel formed is a viscoelastic solid where the gel strength, loss and storage moduli are function of the TMOS concentration.
Biopolymers in enhanced oil recovery

Biopolymers such as starch, xanthan, guar, lignin and cellulose have been used in oil industry for many years. The microorganism Xanthomonas campestris produces xanthan biopolymer. The degradation mechanism of biopolymer like xanthan which is widely used during polymer flooding applications has been explained by Wellington36, Ash et al.37, and Seright and Henrici38. Both biopolymer xanthan and synthetic polymers such as HPAM are susceptible to free-radical attack, which leads to the degradation of the macromolecules.

Foams in water shut-off jobs

In recent years, foam treatment39 has been proved to be effective in gas shut-off jobs in oil wells having high gas/oil ratio (GOR). Foams provide highly attractive alternative over conventional non-Newtonian fluids for various oil and gas industry applications because of their high viscosity and low liquid content. Foams have been successfully used in well stimulations, drilling, acidizing, cleanout operations, and enhanced oil recovery.

Cement plugging to control water production

Cement plugging means the operation whereby a cementing slurry is pumped into a drilled hole and/or forced behind the casing in order to stop the flow of water, oil or gas into or out of a geological formation, group of formations or part of a formation through a borehole or well penetrating these geologic units. In cement plugging operations it is a requirement to have the presence of a workover rig to perform the operation safely and correctly. With gels there is no need of the rig, rather it uses coiled tubing. The penetration depth of polymeric gels is higher compared to cement, allowing for high effectiveness of the treatments. Compatibility of the gel system is better and isolation effectiveness of the gel is not affected by acid40,41.

Stimulation of multilayered reservoirs by in-situ cross-linking acid diverting agent (ISCADA)

Recently Halder et al.27 have found out a new solution to stimulate the multilayered reservoirs by using the in-situ Cross-linking Acid Diverting Agent (ISCADA). This new diverting agent, which is pH and temperature sensitive, can temporary block the high permeable or undesired layers. Water production in some wells has come down remarkably by using ISCADA as diverting agent and substantial improvement in oil productivity has also been observed.

Conclusion

From the above review it can be seen that different methods have been proposed and tested for water controlling jobs in oil producing wells worldwide. We may conclude that:

- Various types of gels that are studied included resorcinol formaldehyde, Cr$^{3+}$ (chloride)-xanthan, Cr$^{3+}$ (acetate)-polyacrylamide and colloidal silica.
- Among these the polymer gels give satisfactory results in almost all types of reservoirs. These gels are used as relative permeability modifiers (RPMs), which reduce the permeability of the water media more than that of the oil, the exact reason of which is still unknown.
- Most of the previous researchers worked with the partially hydrolyzed polyacrylamide gels for water shut-off applications.
- Later studies showed that these gels cross-linked with suitable metal ions such as, trivalent chromium or aluminium give better result in high temperature conditions.
- Recently a new type of silicate gel, TMOS (tetramethoxysilane) reveals a better way of controlling water production during oil recovery.
- Recent studies reveal a new possibility of using in-situ cross-linking acid diverting agent (ISCADA) to stimulate the different layers in the reservoirs and to improve the oil production in certain wells subsequently.
- Selection of a particular type of gel system will depend on the thermal and rheological stability of the gel formed under high temperature/pressure conditions of the reservoir along with the specified reservoir rock and fluid properties.

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