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Hydrogels Applied for Conformance-Improvement Treatment of Oil Reservoirs

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Abstract

This chapter aims at presenting a review of gelling polymer systems that are commercially available or under academic development with potential to control the anisotropic permeability profile of heterogeneous oil reservoirs. In these reservoirs, the oil recovery and sweep efficiency tend to be low, even after applying secondary and enhanced oil recovery methods, because the injected fluid flows preferably through the matrix's most permeable regions leaving behind part of the displaceable oil retained at the nonswept volume. For that, cross-linked polymers can be used to plug the high-permeability main paths by means of: (i) the formation of an *in situ* hydrogel or (ii) the adsorption or swelling of pre-cross-linked hydrogel within the reservoir pores, thus causing the diversion of the subsequently injected fluid to low-permeability zones and/or preventing the channeling and early breakthrough of the injected fluid (water or gas) in production wells. The selection of the most suitable hydrogel for the reservoir conformance-improvement treatment should take into account the nature of the conformance problem, the reservoir's lithology, mineralogy, temperature, pH value, salinity, and hardness of the formation water, as well as the gelling system toxicity and cost.

Keywords: hydrogel, polymer, conformance improvement, reservoir, oil and gas

1. Introduction

During the productive life cycle of an oil reservoir, primary, secondary, and enhanced oil recovery methods can be applied to improve the overall hydrocarbon recovery.

Initially, during primary recovery, the oil production is accomplished by the use of the natural reservoir energy as well as artificial lift and well stimulation methods that do not directly

affect the driving force of the porous medium. Nevertheless, the reservoir primary energy is progressively dissipated due to the decompression of fluids and to forces (viscous and capillary forces) imposed on the matrix flow.

In order to minimize the negative impacts of primary energy dissipation and increase oil recovery, two strategies may be used:

- addition of an artificial secondary energy to the reservoir by means of the injection of fluids, and/or
- reduction of the viscous and/or capillary forces acting on the reservoir.

The injection of fluids into the formation (water or immiscible gas) to displace hydrocarbons from the pores of the reservoir matrix with no chemical or thermodynamic interactions between the injected fluid and oil/reservoir rock is known as secondary recovery.

Together, primary and secondary oil recovery methods produce around 33% of a reservoir's initial-oil-in-place (OOIP) [1]. This low oil recovery inherent in these methods occurs due to: (i) high interfacial tension between oil and injected fluids and/or (ii) high viscous oil in the reservoir¹.

In these cases, the use of enhanced oil recovery (EOR) methods, also known as improved oil recovery (IOR) methods, is recommended, as they act on the sweep efficiency and/or on the displacement efficiency of injected fluids.

However, in fractured and/or stratified reservoirs with anisotropic permeability profiles (conformance problems), the sweep and displacement efficiencies tend to be low even after applying secondary and enhanced oil recovery methods.

In these heterogeneous porous media, the injected fluid tends to flow preferably through high-permeability zones and/or anomalies² (preferential paths), failing to recover part of the displaceable oil in low-permeability-unswept zones of the reservoir.

The channeling of the injected fluid through these high-permeability zones and/or anomalies, besides reducing the total oil recovery, can also be responsible for the early breakthrough of the injected fluid in production wells, thus increasing the operational costs associated with the separation, treatment, and disposal of the produced fluid (e.g. water).

Therefore, to remedy these problems, several authors [2–6] have proposed the injection of gelling polymer systems³ to selectively flow through the high-permeability zones or anomalies, temporarily plugging them with a barrier (hydrogel) (**Figure 1**) in order to:

¹When there is high interfacial tension between the injected fluid and the displaced fluid, the injected fluid capacity to displace oil from the reservoir is significantly reduced, inducing bypass of residual oil by the injected fluid. When the viscosity of the injected fluid is much lower than that of the fluid being displaced, the former displaces much more easily in the porous medium, finding preferential paths and moving quickly toward the producing wells. As the injected fluid does not spread properly inside the reservoir, the oil is trapped in large bulks of reservoir rock in which displacement does not occur.

²Fracture networks (both natural and hydraulically induced), faults, interconnected vugular porosity, caverns, and localized matrix reservoir rock with permeabilities greater than 2 Da.

³The term gelling system or gelant refers to a polymer + cross-linker solution or a microgel dispersion before any appreciable cross-linker has occurred. The term gel is used when the gelling system has attained either partial or full crosslinking maturation.

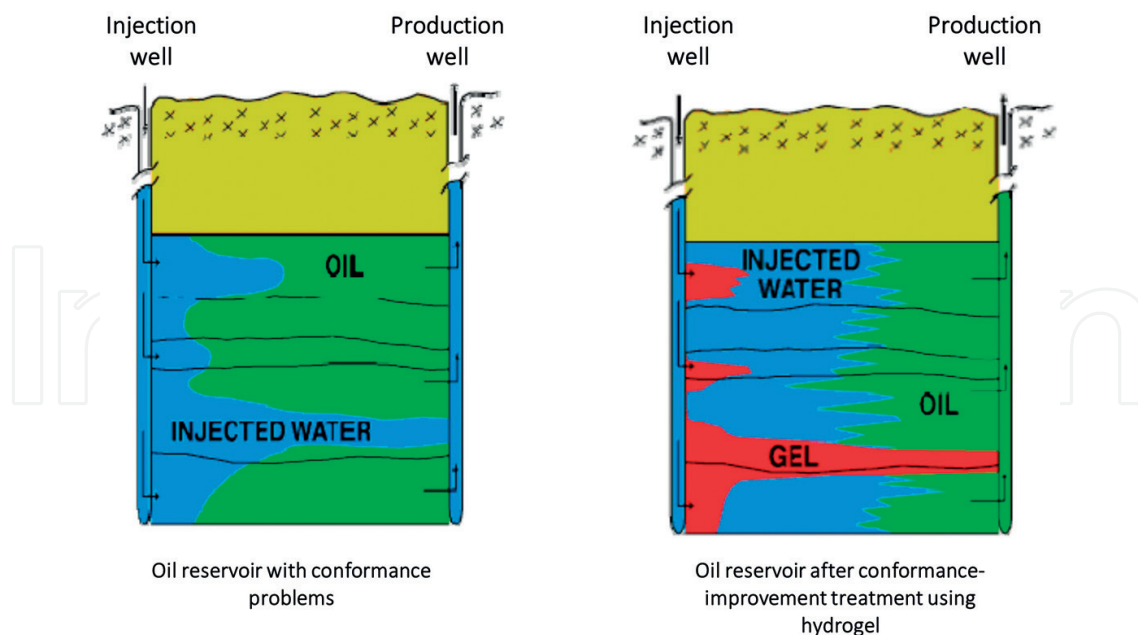


Figure 1. Schematic of an oil reservoir conformance-improvement treatment with hydrogel.

- divert the injected fluid flow from high permeability, low-oil-saturation reservoir flow paths to low-permeability, high-oil-saturation flow paths (in-depth profile control), improving flood sweep efficiency, and producing incremental oil, or
- block high-permeability zones or anomalies located near wellbore modifying the injection profile and/or preventing the channeling and early breakthrough of the injected fluid (water or gas) in production wells (water or gas shut off), thus reducing overall oil-production operational costs.

This chapter aims at presenting a review of gelling polymer systems commercially available or under academic development, with potential to control the anisotropic permeability profile of heterogeneous oil reservoirs.

2. Gelling polymer systems for conformance control of oil reservoirs

Hydrogels used to control the anisotropic permeability profile of oil reservoirs are cross-linked polymers, swellable in water that retain the solvent within their three-dimensional structures without dissolving them [7–9].

Polyacrylamide homopolymer (PAM) and acrylamide copolymers such as: partially hydrolyzed polyacrylamide (PHPA), copoly(acrylamide-*t*-butyl acrylate) (PAtBA), copoly(acrylamide-2-acrylamido-2-methyl-propanesulfonic acid) (PAM-AMPS), and copoly(acrylamide-*N*-vinyl-2-pyrrolidone) (PAM-NVP)⁴ are the most widely used polymers for conformance-improvement

⁴The incorporation of AMPS and/or NVP groups in acrylamide-copolymer chains prevents the acrylamide groups from autohydrolyzing at high temperatures, reducing the polymer susceptibility to precipitate out of the solution in the presence of hardness divalent ions (i.e. Ca^{2+} or Mg^{2+}). For this reason, AMPS-NVP-acrylamide copolymers are mainly applied for the conformance control of reservoirs with harsh conditions (i.e. temperature $> 90^\circ\text{C}$ and salinity $> 100,000$ ppm TDS) [10, 11].

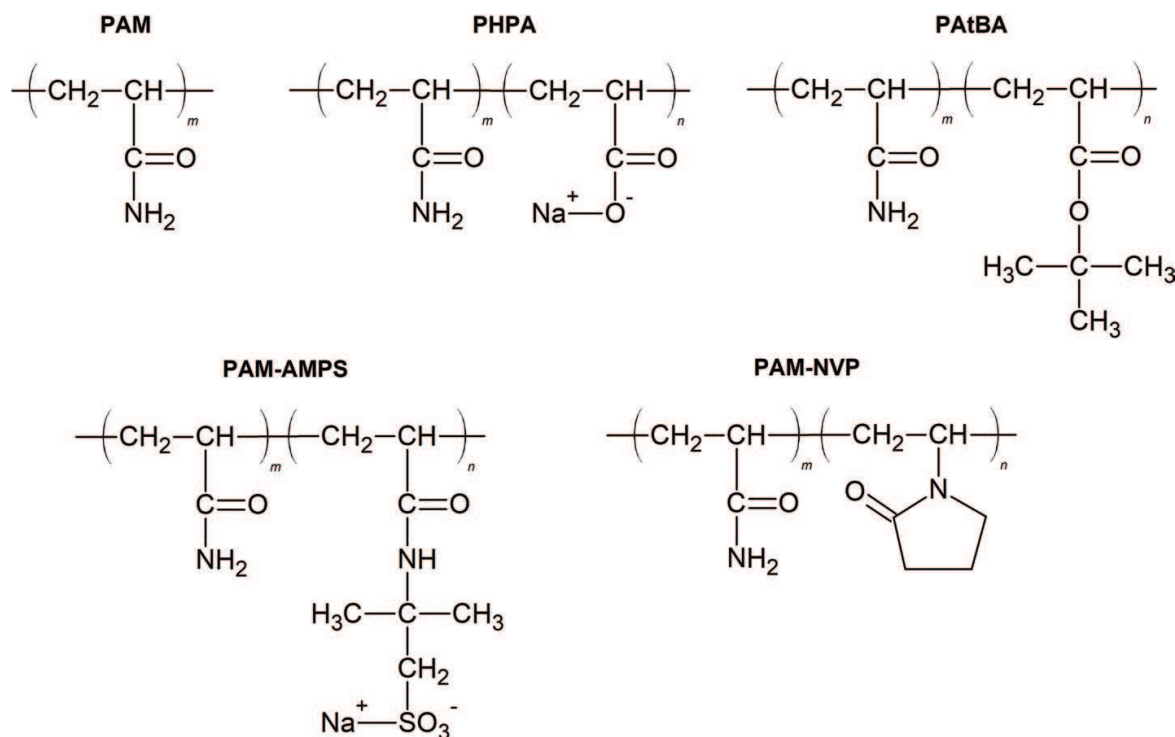


Figure 2. Acrylamide-based polymers used for conformance control of oil reservoirs.

treatments of oil reservoirs **Figure 2**. Biopolymers such as xanthan gum, guar gum, chitosan, starch, cellulose, and scleroglucan have also been studied [7, 11, 12].

These polymers can be cross-linked by organic and inorganic cross-linkers forming chemical hydrogels through covalent bonding or physical hydrogels through ionic complexing, hydrogen bonding, polymer entanglements, van der Waals interactions, and/or hydrophilic interactions [13, 14].

The formed hydrogel structure and properties depend on the gelling system components (polymer, cross-linker, and solvent), the concentration of reagents, and the reaction conditions (pH value, salinity, and temperature). An increase in the polymer and/or cross-linker concentration in the gelling system results in a hydrogel with a rigid structure due to a larger number of cross-links per unit of chain length [13].

For conformance-improvement treatment of heterogeneous oil reservoirs, the gelling system must [11, 12, 15]:

- be formulated with low concentrations of relatively inexpensive environmentally acceptable and friendly chemicals;
- have good injectivity and propagation within the matrix reservoir rock;
- have controllable and predictable gelation time;
- have thermal, mechanical, and biological stability under reservoir conditions; and
- provide a broad range of gel strengths, including rigid gels.

Groups	Gelling polymer systems	Reservoir temperature	Formation water salinity
<i>In situ</i> cross-linked polymer systems	Gelling systems cross-linked with metal ions [11, 20–35]	up to 90°C	up to 30,000 mg/L TDS
	Gelling systems cross-linked with organic compounds [19, 42–57]	30–180°C	30,000–100,000 mg/L TDS
Pre-cross-linked polymer systems	Gelling systems with no cross-linker [58, 59]	up to 90°C	up to 30,000 mg/L TDS
	Colloidal dispersion gels [61–63]	40–90°C	up to 15,000 mg/L TDS
	Microgel systems [4, 64–68]	up to 90°C	insensitive to salinity variations
	BrightWater™ systems [69–73]	35–140°C	up to 120,000 mg/L TDS
	Preformed particle gels [74–76]	up to 120°C	up to 300,000 mg/L TDS
	pH-sensitive gel systems [60, 77–79]	up to 90°C	up to 30,000 mg/L TDS

Table 1. Summary of gelling polymer systems used for conformance control of oil reservoirs.

Furthermore, the porous matrix should present: (i) zones with high-permeability contrasts (e.g. 10:1), (ii) high thickness ratios (e.g. less-permeable zones being 10 times thicker than high-permeability zones, and (iii) relatively low oil viscosities [16].

Moreover, hydrogels that suffer severe dehydration and syneresis, greatly reducing their volume over time under reservoir conditions, are not suitable for reservoir permeability profile treatments⁵.

Several gelling systems have been developed (**Table 1**) for the treatment of high-permeability zones of a broad range of reservoir conditions⁶ by means of the:

- formation of an *in situ* hydrogel (Section 2.1); or
- adsorption/swelling of pre-cross-linked hydrogel within the reservoir rock (Section 2.2).

2.1. *In situ* cross-linked polymer systems

In *in situ* cross-linked polymer systems, a polymer solution and a cross-linking agent are injected together into the porous matrix forming an *in situ* hydrogel within the high-permeability zones of the reservoir [19–22].

⁵Gel dehydration can occur in fractures subjected to high pressure gradients. Gel syneresis can result from the increase in the cross-linking density due to excessive cross-linker agent addition and/or excessive cross-linking sites developed on the polymer chain overtime (e.g. autohydrolysis of acrylamide polymers at high temperatures) [17].

⁶Typical conditions found in oil reservoirs are: temperature ranging from 50 to 150°C, pressure between 10 and 50 MPa, salinity from 2000 up to 300,000 mg/L of Total Dissolved Solids (TDS) (with 1 to 35 mg/L of divalent ions), pH value between 4 and 8, and permeability from 10 to 450 mD [18].

Several cases of success of field applications of *in situ* cross-linked gelling systems have been reported for the conformance-improvement treatment of high-permeability zones located near-wellbore (with radial penetration into the matrix lower than 5 m) and far-wellbore (with radial penetration into the matrix greater than 5 m). However, *in situ* cross-linked gelling systems still face a number of operational difficulties regarding the control of the gelation kinetics, the efficient mixing of the polymer and cross-linker within the reservoir, the prevention of undesirable separation of the gelant components into the heterogeneous matrix, and the risk of plugging the whole formation or areas containing oil [23].

The major *in situ* cross-linked polymer systems commercially available or under academic development are presented below.

2.1.1. Gelling systems cross-linked with metal ions

A wide variety of metal ions (e.g. chromium (III), aluminum (III), zirconium (IV), and titanium (III)) can be used to cross-link water-soluble polymers with carboxylates groups such as: polyacrylamide copolymers (e.g. PHPA, PAtBA, and PAM-AMPS) and biopolymers (e.g. xanthan gum, starch, guar, carboxymethylcellulose, scleroglucan, and lignosulfonates) [11, 20].

These gelling systems form physical bulk hydrogels with continuous semi-solid three-dimensional structures by means of ionic interactions between the multivalent metal cations of the cross-linker and the carboxylate/anions of the polymer chains. The cross-linking rates of these systems can be controlled by varying the polymer and cross-linker concentration, the polymer hydrolysis degree, the solution pH value, and by adding cross-linker's retardants (e.g. acetates, propionates, malonates, and ascorbates) [11, 24–26].

PHPA-chromium (III) ions-based formulations are one of the most commonly used systems applied for the permeability profile treatment of oil reservoirs. These systems have been studied extensively as well as tested in laboratory and field for in-depth conformance control of reservoirs with temperatures up to 90°C [27, 28].

Routson and Caldwell [29] were the first to observe that the injection of a dilute solution of chromium hydroxide and PHPA into a porous medium formed a gel that reduced the matrix permeability. Several authors have proposed changes in the formulation developed by Routson and Caldwell [29] in order to reduce the gelant environmental impact, to increase the gelation time, as well as to improve the formed hydrogel strength and stability such as:

- the use of alternative metal ions with lower toxicity when compared to chromium (III) ions, for example, aluminum (III), zirconium (IV), and titanium (III) ions [11, 30–32];
- the use of metal ions retardants to increase the gelant gelation time, for example, acetates, propionates, malonates, and ascorbates [17, 32–35]. Malonate ions are 33 times slower than acetate ions in the gelation of PAM-AMPS at 120°C. Under the same conditions, ascorbate ions are 51 times slower than acetate ions. Nevertheless, the use of complexes of metal ions results in the formation of weak hydrogels [34];

- the encapsulation of the cross-linker by polyelectrolyte nanogels of polyethylenimine (PEI) and dextran sulfate (DS) to control the release of the metal ions into the porous matrix, forming hydrogels with gelation time from 5 to 30 days, depending on the reservoir temperature [36, 37];
- the use of biopolymers less shear-sensitive than the polyacrylamide in chromium (III)-cross-linked formulations to reduce the polymer degradation when subjected to prolonged shear into the reservoir, for example, xanthan gum, scleroglucan, *Alcaligenes* bacteria-produced biopolymer and lignosulfonate by-product from paper industry [38, 39]; and
- the addition of nanoclays (e.g. kaolinite, laponite, and montmorillonite) to the PHPA/PAM-AMPS-chromium (III) acetate formulations forming nanocomposite hydrogels with good mechanical strength (modulus, elasticity, and deformability) and improved syneresis resistance [40, 41].

2.1.2. Gelling systems cross-linked with organic compounds

Various organic compounds (e.g. phenol, resorcinol and formaldehyde, hydroquinone, hexamethylenetetramine, chitosan, modified starch and polyethylenimine) can be used to cross-link water-soluble acrylamide-based polymers (e.g. PAM, PHPA, PAtBA, PAM-AMPS, and PAM-NVP) and biopolymers (e.g. modified starch and chitosan) [11, 20, 42–46].

In these systems, a chemical bulk hydrogel with continuous semi-solid three-dimensional network is formed by the reaction of the cross-linker functional groups with the polymer chain functional groups through covalent bonding. These systems have been extensively studied and tested in laboratory and field, especially for harsh reservoir environments (high temperature, salinity, and/or pH value). They have higher gelation times and form hydrogels with higher thermal stability when compared to metal ion-cross-linked systems and are used for the conformance-improvement treatment of reservoirs with temperatures around 30 up to 180°C [43, 47–49].

Polyacrylamide cross-linked with the product of phenol-formaldehyde reaction formed a hydrogel that remained stable for 13 years at 121°C in a laboratory aging test. This gelling system was successfully applied for the treatment of oil reservoir conformance problems [7, 50].

Despite the good thermal stability shown under harsh conditions, phenol-formaldehyde cross-linked gelling systems have great disadvantages, the phenol toxicity and the formaldehyde carcinogenicity. Thus, less toxic and more environmentally friendly organic cross-linking agents have been studied.

Ortho and para-aminobenzoic acids, m-aminophenol, phenyl acetate, phenyl salicylate, salicylamide, salicylic acid, and furfuryl alcohol were identified as substitutes for phenol and hexamethylenetetramine (HMTA) proved to be suitable to replace formaldehyde, forming stable hydrogels with polyacrylamide [51].

Gelling systems based on polyacrylamide cross-linked with hydroquinone (HQ), hexamethylenetetramine (HMTA), and sodium bicarbonate-formed hydrogels that remained stable for 12 months, at 149°C, and for 5 months, at 176.7°C [52, 53].

The performance of gelling systems based on acrylamide copolymers and biopolymers (starch and chitosan) cross-linked with chitosan, starch, and polyethylenimine (PEI) has been evaluated for the conformance control of reservoir with temperatures above 80°C. Laboratory tests showed that PAtBA cross-linked with PEI formed a stable hydrogel at 156°C for 3 months. Furthermore, acrylamide-based polymers-PEI systems were successfully applied to treat conformance problems of carbonate and sandstone reservoirs with temperatures around 130 and 80°C, respectively [47, 49, 54–57].

2.1.3. Gelling systems with no cross-linker

Kansas University Super Polymer One (KUSP1) is a gelling system developed by the University of Kansas based on a biopolymer-polysaccharide (β -1,3-polyglucane)—produced via fermentation by *Alcaligenes faecalis* and *Agrobacterium* bacteria.

This nontoxic biopolymer gels in the absence of cross-linker when the pH value is reduced below 10.8. This gelation process is reversible so that the formed hydrogel can be dissolved by increasing the pH of the solution and can be re-gelled by reducing it.

Field tests were carried out with KUSP1 gelling system to control the permeability profile of oil reservoirs [58, 59].

2.2. Pre-cross-linked polymer systems

In pre-cross-linked polymer systems, the polymer chains are cross-linked in the surface facilities prior to be injected into the reservoir, or at least, are partially gelled in the wellbore. These systems are injected into the reservoir in the form of dispersed aggregates or particles that swell in water within the matrix plugging thief zones with high permeability.

These dispersed aggregates or preformed particles do not have the same drawbacks faced by the *in situ* cross-linked systems, such as: reaction control problems, change of gelant composition or dilution by the formation water. However, the pre-cross-linked gelling systems may undergo high mechanical retention and filtration through the pores of the reservoir, increasing the pressure losses of the system, and may face operational issues associated with poor injectivity of the swollen particles and risk of plugging undesired regions of the reservoir matrix.

Several cases of success of field applications of pre-cross-linked polymer systems have been reported for the conformance control of high-permeability zones and anomalies located near-wellbore or deeply into the matrix reservoir rock. The injection of preformed gel particles into the reservoir prevents these systems from substantially invading and damaging the matrix rock adjacent to the treated zone [4, 60].

The major pre-cross-linked polymer systems commercially available or under academic development are presented below. The main differences between them are related to particle sizes, swelling rates, and reservoir conditions in which they can be applied.

2.2.1. Colloidal dispersion gels (CDG)

Colloidal dispersions gels (CDGs) are microgel aggregates that are formed cross-linking a low concentration solution of polymer (e.g. PHPA and PAM-AMPS) with metal ions (e.g. aluminum

citrate or chromium citrate). The low polymer concentrations used in these systems are not enough to form a continuous three-dimensional network, and thus, they produce a dispersion of separate gel bundles in which predominate intramolecular cross-links [61–63].

CDG treatments involve the injection of large volumes of microgel aggregates into the formation. Nevertheless, the low polymer concentrations used in their formulation make them cost-effective.

The mechanism by which CDG treatment generates incremental oil production is not fully understood. Laboratory and field tests carried out in the USA and China showed good results for the in-depth conformance control of high-permeability zones of sandstone reservoirs [62].

2.2.2. Microgel systems

Microgel systems are micrometer-sized particle gels that are prepared cross-linking a acrylamide terpolymer (with 2% of acrylate and 2% of sulfonate groups) with zirconium (IV) ions and lactate (used as a chelater) or with chromium (III) ion and acetate, under defined shear conditions, to control the microgel globule size (1–10 μm) [4, 64–67].

In these systems, the reservoir permeability control is accomplished by the adsorption of the flexible microgel globules onto the pore walls of the reservoir rock, forming monolayers with thickness equal to the diameter of the gel microspheres. The plugging of the porous medium can be controlled by the appropriate selection of the dimension of the microspheres used for the reservoir treatment.

Some successful field tests were conducted with these flexible microgels for the permeability profile control of Daqing reservoir (China) [68].

2.2.3. BrightWater™ systems

BrightWater™ systems are commercial submicro-sized particle gels based on sulfonate-acrylamide-polymers (PAM-AMPS) with both labile and stable cross-links. These systems are prepared using an inverse emulsion polymerization process in order to control the particles size distribution in a sub-micron range ($<1 \mu\text{m}$). Surfactants are also added into the formulation to fully disperse the micro- or nano-sized particles avoiding them to agglomerate.

These pre-cross-linked systems, developed by MobPTECh and Ondo Nalco Energy Services, can be applied for in-depth conformance treatment of reservoirs with temperatures between 35 and 140°C and salinity up to 120,000 mg/L TDS [69, 70].

When BrightWater™ particles are injected into the reservoir, they encounter high temperatures and swell irreversibly (pop up) through the cleavage of the labile cross-links. The cross-linking density of the particle gels decreases allowing them to expand aggressively by absorbing additional water, blocking the high-permeability zones. After the labile cross-links dissociation, the stable cross-links maintain the particle gel network and prevent hydrolysis [69, 70].

After thermal activation, the particles of the BrightWater™ system expand approximately 10 times their original size. The cleavage rate control of the labile cross-links at different temperatures can be made through the appropriate selection of the cross-linking agent used for the submicrogel synthesis [71].

Field tests, both onshore and offshore, carried out in North America, Asia, Africa, Europe, and South America, showed that BrightWater™ submicrogels can travel long distances, allowing the permeability control of the reservoir at great depths [69, 71–73].

2.2.4. *Preformed particle gels (PPG)*

Preformed particle gels (PPG) and partially preformed gel systems are millimeter-sized preformed gels (10 μm to mm) based on acrylamide, polyacrylamide copolymers (e.g. PAM, PHPA, PAtBA, and PAM-AMPS), modified superabsorbent polymers (SAP), or biopolymers (e.g. chitosan and starch) cross-linked with metal ions (e.g. chromium acetate), organic compounds (e.g. N-N'-methylene-bis-acrylamide and PEI) or biopolymers (e.g. chitosan and starch) [74, 75].

The PPGs are prepared by solution polymerization/cross-linking followed by drying, crushing, and sieving the preformed bulk gels to the desired particle size. In the field, prior to be injected into the reservoir, these preformed particles swell in water forming strong and stable hydrogels in surface facilities [74–76].

PPGs were applied in China for more than 2000 wells to reduce the water production in mature water-flooded reservoirs. Since PPGs particles are relatively large, their application is limited to reservoirs with fractures or fracture-like channels.

The PPGs have many advantages over other conformance-improvement treatments, such as [74, 76]:

- good size distribution control of particles (μm –cm);
- insensitivity to reservoir minerals and formation water salinity;
- high thermal and chemical stability at temperatures up to 120°C and salinities up to 300,000 mg/L TDS (including multivalent cations); and
- ease preparation in surface facilities (e.g. produced water can be used to prepare them).

In order to improve the PPG swellability, thermal stability and mechanical strength (modulus, elasticity, and deformability) nanoclays (e.g. kaolinite, laponite, and montmorillonite) can be added to their formulation [75].

2.2.5. *pH-sensitive gel systems*

pH-sensitive gel systems are micrometer-sized particle gels (1–10 μm) that are based on anionic polyelectrolytes (e.g. PHPA and poly(acrylic acid)) cross-linked by allyl ethers of polyols (e.g. allyl pentaerythritol).

In these systems, the pre-cross-linked microgels injection is carried out at low pH values. The pre-addition of hydrochloric acid or citric acid is necessary to reduce the viscosity of the microgels before injection – the low-pH coils polymer chains reducing the gelant viscosity. Once deep into the reservoir, the gel microglobules swell (polymer chains uncoil absorbing

formation water) due to the increase of the pH caused by geochemical reactions between the acid (injected with the microgel) and the mineral components of the matrix rock [77].

The microgel swelling-deswelling process occurs due to electrostatic effects caused by adjacent anionic groups that change the hydrodynamic volume of the macromolecules and their conformation in solution [77, 78].

Laboratory and field tests with pH-sensitive gel systems were successfully carried out for in-depth conformance control of reservoirs [60, 79].

3. Gelling polymer system screening

The success of a hydrogel-conformance-improvement treatment depends on the correct assessment of the nature of the conformance problem and on the selection of an effective gelling system.

Reservoir conformance problems that can be treated with gelling polymer systems are basically [21, 22]:

- **Matrix conformance problems**—high-permeability flow path (with no cross-flow) occurring through an unfractured matrix rock with permeability lower than 2 Da. For those, the gelling system is injected into the reservoir, preferably in the gelant state, from the injection well side, improving the overall flood sweep efficiency and generating incremental oil production;
- **Anomaly conformance problems**—high-permeability flow path and/or water/gas coning occurring through anomalies such as: fracture networks (both natural and hydraulically induced), faults, interconnected vugular porosity, caverns, and localized matrix reservoir rock with permeabilities greater than 2 Da. For those, the gelling system is injected into the reservoir, preferably in a matured or partially matured state, from: (i) the production well side for water/gas-shutoff treatments near-wellbore purely blocking the fluid flow, or (ii) the injection well side for the placement of the hydrogels in some significant distance into the fracture or other anomaly surrounding the injection well, functioning as a plugging and diverting agent.

The screening and selection of the most appropriate gelling polymer system for the conformance-improvement treatment of an oil reservoir can be done using different laboratory tests (i.e. bottle tests, continuous and oscillatory rheological measures, and core flooding experimental tests) to access information on the gelation time and final gel strength, as well as the short- and long-term stability of gelling polymer systems under specific reservoir conditions – temperature, salinity, pH value of the formation water, and the presence of either carbon dioxide (CO₂) or hydrogen sulfide (H₂S) [20, 35, 53, 80–83].

Gelling polymer systems used to control the anisotropic permeability profile of oil reservoir should:

- behave as moderately pseudoplastic fluids, with viscosity between 10 and 30 mPa.s at a constant shear rate of 7 s⁻¹ to ensure good injectivity and propagation in the porous medium.

These injectivity and propagation parameters can be obtained by continuous rheological tests [56, 84, 85];

- have controllable gelation times, preferably greater than 2 hours, to avoid overloads in the unit's pumping system during the injection of the gelant in the reservoir. Furthermore, the gelation time must be long enough for the gelling system to reach the proposed targets (high-permeability zones or anomalies). This injectivity and propagation parameter can be obtained by bottle tests and continuous and oscillatory rheological tests [45];
- form strong hydrogel under reservoir conditions-with Sydansk's gel-strength code $> G$ (bottle testing, **Figure 3**), elastic modulus (G'), and viscous modulus (G'') ratio above 10 ($G'/G'' > 10$) with G' and G'' being independent of the oscillation frequency, and $G' > 1$ Pa. These blocking-ability parameters can be obtained by bottle tests and oscillatory rheological tests [9, 20, 42, 56, 86];
- provide permeability reduction factor (PRF) above 1 after the matrix treatment with the hydrogel. This blocking-ability parameter can be obtained by core flooding experimental tests [78].

Other parameters that should also be considered during the screening are the toxicity and cost of the gelling system components, as well as their thermal, mechanical, and biological stability, retention, and adsorption on reservoir rock.

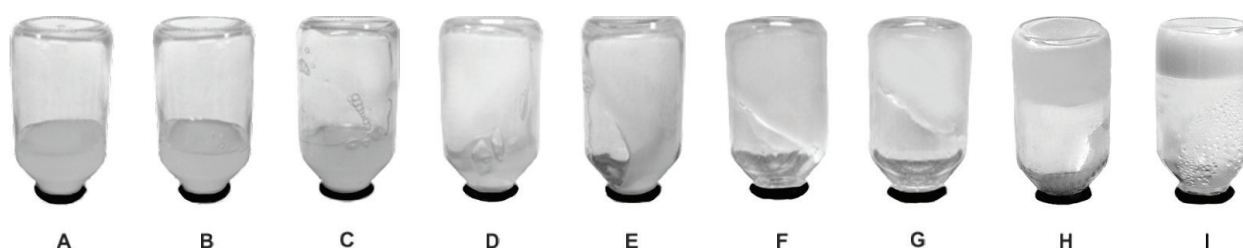


Figure 3. Bottle testing characterization of PAM-PEI hydrogels using the Sydansk's gel-strength code.

4. Conclusion

A large amount of gelling polymer systems applicable for the conformance-improvement treatment of heterogeneous oil reservoirs is commercially available or under academic development.

Choosing the most suitable hydrogel for a conformance problem should be done taking into account the temperature, salinity, and hardness of the reservoir, as well as the pH of the injection water.

Other parameters that should also be considered are the presence of carbon dioxide (CO_2) or hydrogen sulfide (H_2S), the adsorption of the chemicals on reservoir rock, the permeability of the target region, reservoir mineralogy and lithology, as well as toxicity and cost of the gelling system components.

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References

- [1] Sydansk RD, Romero-Zerón L. Reservoir conformance improvement. Richardson: Society of Petroleum Engineers; 2011
- [2] Liu Y, Bai B, Wang Y. Applied technologies and prospects of conformance control treatments in China. *Oil and Gas Science and Technology D'IFP Energies Nouvelles*. 2010;**65**(6):859-878
- [3] Kabir AH. Chemical water & gas shutoff technology: An overview. In: SPE Asia Pacific Improved Oil Recovery Conference, SPE-72119-MS. 2001
- [4] Feng Y, Tabary R, Renard M, Le Bon C, Omari A, Chauveteau G. Characteristics of microgels designed for water shutoff and profile control. In: International Symposium on Oilfield Chemistry, SPE-80203-MS. 2003
- [5] Hu S, Zhang LH, Yu HJ, Wei W, Luo J. Development and prospect of the profile control/water shutoff technology in reservoir high-capacity channels. *Drilling and Production Technology*. 2006;**29**(6):117
- [6] Ma S, Dong M, Li Z, Shirif E. Evaluation of the effectiveness of chemical flooding using heterogeneous sandpack flood test. *Journal of Petroleum Science and Engineering*. 2007;**55**(3):294-300
- [7] Moradi-Araghi A. A review of thermally stable gels for fluid diversion in petroleum production. *Journal of Petroleum Science and Engineering*. 2000;**26**(1):10
- [8] Sengupta B, Sharma VP, Udayabhanu G. Gelation studies of an organically cross-linked polyacrylamide water shut-off gel system at different temperatures and pH. *Journal of Petroleum Science and Engineering*. 2012;**81**:145-150
- [9] Tokita M, Nishinari K. Gels: structures, properties, and functions: Fundamentals and applications. Vol. 136. Springer-Verlag Berlin Heidelberg; 2009
- [10] Doe PH, Moradi-Araghi A, Shaw JE, Stahl GA. Development and evaluation of EOR polymers suitable for hostile environments Part 1: Copolymers of vinylpyrrolidone and acrylamide. *SPE Reserv Eng SPE-14233-PA*. 1987;**2**(04):461-467
- [11] Vossoughi S. Profile modification using in situ gelation technology — A review. *Journal of Petroleum Science and Engineering*. 2000;**26**(1):199-209

- [12] Al-Muntasheri GA. Conformance control with polymer gels: What it takes to be successful. *Arabian Journal for Science and Engineering*. 2012;**37**(4):1131-1141
- [13] Gehrke SH. Synthesis, equilibrium swelling, kinetics, permeability and applications of environmentally responsive gels. In: *Responsive Gels: Volume Transitions II*. Springer; 1993. p. 81-144
- [14] Zhao H, Zhao P, Xiao L, Liu X, Bai B. Using associated polymer gels to control conformance for high temperature and high salinity reservoirs. *Journal of Canadian Petroleum Technology*. 2006;**45**(5):49-54
- [15] Vasquez J, Eoff L. Laboratory development and successful field application of a conformance polymer system for low-, medium-, and high-temperature applications. In: *SPE Latin American and Caribbean Petroleum Engineering Conference*, SPE-139308-MS. Society of Petroleum Engineers; 2010
- [16] Seright R, Zhang G, Akanni O, Wang D. A comparison of polymer flooding with in-depth profile modification. *Journal of Canadian Petroleum Technology*. 2012;**51**(05):393-402
- [17] Albonico P, Lockhart TP. Stabilization of polymer gels against divalent ion-induced syneresis. *Journal of Petroleum Science and Engineering*. 1997;**18**(1):61-71
- [18] Donaldson EC, Chilingarian GV, Yen TF. Enhanced oil recovery, I: Fundamentals and analyses. Amsterdam, Netherlands: Elsevier; 1985. e-book ISBN: 9780080868721
- [19] Vasquez J. Laboratory evaluation of high-temperature conformance polymer systems. M. Sc. Thesis. University of Oklahoma; 2004
- [20] Sydansk RD. A new conformance-improvement-treatment chromium (III) gel technology. In: *SPE Enhanced Oil Recovery Symposium*. Society of Petroleum Engineers; 1988
- [21] Sydansk RD, Southwell GP. More than 12 years' experience with a successful conformance-control polymer-gel technology. *SPE Prod Facil* SPE-66558-PA. 2000;**15**(04):270-278
- [22] Seright RS, Lane RH, Sydansk RD. A strategy for attacking excess water production. In: *SPE Permian Basin Oil and Gas Recovery Conference*, SPE-70067-MS. Society of Petroleum Engineers; 2001
- [23] Seright RS, Liang J. A survey of field applications of gel treatments for water shut-off. In: *SPE Latin America/Caribbean Petroleum Engineering Conference*, SPE-26991-MS. Society of Petroleum Engineers; 1994
- [24] Tackett JE. Hydrolyzed polyacrylamide/chromium (III) acetate gel chemistry. *Applied Spectroscopy*. 1991;**45**(10):1674-1678
- [25] Ricks Jr GV, Portwood JT. Injection-side application of MARCIT polymer gel improves waterflood sweep efficiency, decreases water-oil ratio, and enhances oil recovery in the McElroy Field, Upton County, Texas. In: *SPE Permian Basin Oil and Gas Recovery Conference*, SPE-59528-MS. Society of Petroleum Engineers; 2000

- [26] Portwood JT. The Kansas Arbuckle formation: performance evaluation and lessons learned from more than 200 polymer-gel water-shutoff treatments. In: SPE Production Operations Symposium, SPE-94096-MS. Society of Petroleum Engineers; 2005
- [27] Norman C, Turner B, Romero J, Centeno G, Muruaga E. A review of over 100 polymer gel injection well conformance treatments in Argentina and Venezuela: Design, field implementation and evaluation. In: First International Oil Conference and Exhibition in Mexico, SPE-101781-MS. Society of Petroleum Engineers; 2006
- [28] Willhite GP, Pancake RE. Controlling water production using gelled polymer systems. SPE Reservoir Evaluation and Engineering SPE-89464-PA. 2008;**11**(03):454-465
- [29] Routson WG, Caldwell AL. Method and composition for controlling flow through subterranean formations. US Patent 3,701,384; 1972
- [30] Dovan HT, Hutchins RD. Development of a new aluminum/polymer gel system for permeability adjustment. SPE Reservoir Evaluation and Engineering SPE-12641-PA. 1987;**2**(02):177-183
- [31] Needham RB, Threlkeld CB, Gall JW. Control of water mobility using polymers and multivalent cations. In: SPE Improved Oil Recovery Symposium, SPE-4747-MS. Society of Petroleum Engineers; 1974
- [32] Ghazali HA, Willhite GP. Permeability modification using aluminum citrate/polymer treatments: Mechanisms of permeability reduction in sandpacks. In: SPE Oilfield and Geothermal Chemistry Symposium, SPE-13583-MS. Society of Petroleum Engineers; 1985
- [33] Lockhart TP, Albonico P. A new gelation technology for in-depth placement of Cr³⁺/polymer gels in high-temperature reservoirs. SPE Prod Facil SPE-24194-PA. 1994;**9**(04): 273-279
- [34] Albonico P, Burrafato G, Di Lullo A, Lockhart TP. Effective gelation-delaying additives for Cr³⁺/polymer gels. In: SPE International Symposium on Oilfield Chemistry, SPE-25221-MS. Society of Petroleum Engineers; 1993
- [35] Stavland A, Nilsson S. Delayed gelation in corefloods using Cr (III)-malonate as a cross-linker. Journal of Petroleum Science and Engineering. 1995;**13**(3):247-258
- [36] Cordova M, Cheng M, Trejo J, Johnson SJ, Willhite GP, Liang J-T, et al. Delayed HPAM gelation via transient sequestration of chromium in polyelectrolyte complex nanoparticles. Macromolecules. 2008;**41**(12):4398-4404
- [37] Johnson S, Trejo J, Veisi M, Willhite GP, Liang J-T, Berkland C. Effects of divalent cations, seawater, and formation brine on positively charged polyethylenimine/dextran sulfate/chromium (III) polyelectrolyte complexes and partially hydrolyzed polyacrylamide/chromium (III) gelation. Journal of Applied Polymer Science. 2010;**115**(2):1008-1014

- [38] Abdo MK, Chung HS, Phelps CH, Klaric TM. Field experience with floodwater diversion by complexed biopolymers. In: SPE Enhanced Oil Recovery Symposium, SPE-12642-MS. Society of Petroleum Engineers; 1984
- [39] Rivenq RC, Donche A, Nolk C. Improved scleroglucan for polymer flooding under harsh reservoir conditions. SPE Reservoir Engineering. 1992;7(01):15-20
- [40] Zolfaghari R, Katbab AA, Nabavizadeh J, Tabasi RY, Nejad MH. Preparation and characterization of nanocomposite hydrogels based on polyacrylamide for enhanced oil recovery applications. Journal of Applied Polymer Science. 2006;100(3):2096-2103
- [41] Salimi F, Sefti MV, Jarrahan K, Rafipoor M, Ghorashi SS. Preparation and investigation of the physical and chemical properties of clay-based polyacrylamide/Cr (III) hydrogels as a water shut-off agent in oil reservoirs. Korean Journal of Chemical Engineering. 2014;31(6):986-993
- [42] Wang W, Liu Y, Gu Y. Application of a novel polymer system in chemical enhanced oil recovery (EOR). Colloid & Polymer Science. 2003;281(11):1046-1054
- [43] Morgan JC, Smith PL, Stevens DG. Chemical adaptation and deployment strategies for water and gas shut-off gel systems. In: Royal Chemistry Society's Chemistry in the Oil Industry 6th International Symposium. Ambleside, UK. 1997. p. 14-17
- [44] Hutchins RD, Dovan HT, Sandiford BB. Field applications of high temperature organic gels for water control. In: SPE/DOE Improved Oil Recovery Symposium. Society of Petroleum Engineers; 1996
- [45] Jayakumar S, Lane R. Delayed crosslink polymer flowing gel system for water shut-off in conventional and unconventional oil and gas reservoirs. In: SPE International Symposium and Exhibition on Formation Damage Control, SPE-151699-MS. 2012
- [46] Reddy BR, Eoff L, Dalrymple E, Black K, Brown D, Rietjens M. A natural polymer-based cross-linker system for conformance gel systems. SPE Journal. 2003;8(2):99-106
- [47] Eoff L, Dalrymple E, Everett D, Vasquez J. Worldwide field applications of a polymeric gel system for conformance applications. SPE Production & Operations. 2007;22(2):231-235
- [48] ElKarsani KSM, Al-Muntasheri GA, Hussein IA. Polymer systems for water shut-off and profile modification: A review over the last decade. SPE J SPE-163100-PA. 2014;19(01):135-149
- [49] Al-Muntasheri G, Nasr-El-Din H, Zitha P. Gelation kinetics and performance evaluation of an organically crosslinked gel at high temperature and pressure. SPE Journal. 2008;13(3):337-345
- [50] Albonico P, Bartosek M, Malandrino A, Bryant S, Lockhart TP. Studies on phenol-formaldehyde crosslinked polymer gels in bulk and in porous media. In: International Symposium on Oilfield Chemistry. 1995. p. 403-415

- [51] Moradi-Araghi A. Application of low-toxicity crosslinking systems in production of thermally stable gels. In: SPE/DOE Improved Oil Recovery Symposium, SPE-27826-MS. Society of Petroleum Engineers; 1994
- [52] Sengupta B, Sharma VP, Udayabhanu G. In-situ gelation studies of an eco-friendly cross-linked polymer system for water shut-off at high temperatures. *Energy Sources Part Recovery Utilization, and Environmental Effects*. 2014;**36**(13):1445-1467
- [53] Yadav US, Mahto V. Rheological investigations of partially hydrolyzed polyacrylamide–hexamine–hydroquinone gel. *International Journal*; 2013
- [54] Hardy M, Botermans W, Hamouda A, Valdal J, Warren J. The first carbonate field application of a new organically crosslinked water shutoff polymer system. In: SPE International Symposium on Oilfield Chemistry. 1999. p. 361-376
- [55] Jia H, Pu W-F, Zhao J-Z, Jin F-Y. Research on the gelation performance of low toxic PEI cross-linking PHPAM gel systems as water shutoff agents in low temperature reservoirs. *Industrial and Engineering Chemistry Research*. 2010;**49**(20):9618-9624
- [56] ElKarsani KSM, Al-Muntasheri GA, Sultan AS, Hussein IA. Performance of PAM/PEI gel system for water shut-off in high temperature reservoirs: Laboratory study. *Journal of Applied Polymer Science*. 2015;**132**(17)
- [57] Vasquez J, Dalrymple ED, Eoff L, Reddy BR, Civan F. Development and evaluation of high-temperature conformance polymer systems. In: SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers; 2005
- [58] Shaw A. Study of permeability modification by in-situ gelation of KUSP1-monoethylphthalate ester system in porous media. M. Sc. Thesis. Lawrence, KS: University of Kansas; 1995
- [59] Fichadia A. Survey of gelation systems and a study of the gelation of KUSP1 by hydrolysis of mono-ethyl phthalate. M.C Thesis. University of Kansas; 1995
- [60] Choi SK. A study of a pH-sensitive polymer for novel conformance control applications. Univ Tex Austin; 2005
- [61] Smith JE. Performance of 18 polymers in aluminum citrate colloidal dispersion gels. In: SPE International Symposium on Oilfield Chemistry, SPE-28989-MS. Society of Petroleum Engineers; 1995
- [62] Chang HL, Sui X, Xiao L, Guo Z, Yao Y, Yiao Y, et al. Successful field pilot of in-depth colloidal dispersion gel (CDG) technology in Daqing Oilfield. *SPE Reservoir Evaluation and Engineering* SPE-89460-PA. 2006;**9**(06):664-673
- [63] Al-Assi AA, Willhite GP, Green DW, McCool CS. Formation and propagation of gel aggregates using partially hydrolyzed polyacrylamide and aluminum citrate. *SPE Journal*. 2009;**14**(03):450-461

- [64] Chauveteau G, Tabary R, Le Bon C, Renard M, Feng Y, Omari A, et al. In-depth permeability control by adsorption of soft size-controlled microgels. In: SPE European Formation Damage Conference, SPE-82228-MS. Society of Petroleum Engineers; 2003
- [65] Chauveteau G, Omari A, Tabary R, Renard M, Rose J. Controlling gelation time and microgel size for water shutoff. In: SPE/DOE Improved Oil Recovery Symposium, SPE-59317-MS. Society of Petroleum Engineers; 2000
- [66] Zaitoun A, Tabary R, Rousseau D, Pichery TR, Nouyoux S, Mallo P, et al. Using microgels to shut off water in a gas storage well. In: International Symposium on Oilfield Chemistry, SPE-106042-MS. Society of Petroleum Engineers; 2007
- [67] Cozic C, Rousseau D, Tabary R. Broadening the application range of water shutoff/conformance-control microgels: An investigation of their chemical robustness. In: SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, SPE-115974-MS; 2008
- [68] Xia H, Wang D, Wu W, Jiang H. Effect of the viscoelasticity of displacing fluids on the relationship of capillary number and displacement efficiency in weak oil-wet cores. In: Asia Pacific Oil and Gas Conference and Exhibition, SPE-109228-MS. Society of Petroleum Engineers; 2007
- [69] Frampton H, Morgan JC, Cheung SK, Munson L, Chang KT, Williams D. Development of a novel waterflood conformance control system. In: SPE/DOE Symposium on Improved Oil Recovery, SPE-89391-MS. Society of Petroleum Engineers; 2004
- [70] Salehi M, Thomas CP, Kevwitch R, Garmeh G, Manrique EJ, Izadi M. Performance evaluation of thermally-activated polymers for conformance correction applications. In: SPE Improved Oil Recovery Symposium, SPE-154022-MS. Society of Petroleum Engineers; 2012
- [71] Ohms D, McLeod JD, Graff CJ, Frampton H, Morgan JC, Cheung SK, et al. Incremental-oil success from waterflood sweep improvement in Alaska. SPE Production and Operations SPE-121761-PA. 2010;25(03):247-254
- [72] Mustoni J, Denyer P, Norman C. Deep conformance control by a novel thermally activated particle system to improve sweep efficiency in mature waterfloods of the San Jorge basin. In: SPE Improved Oil Recovery Symposium, SPE-129732-MS. Society of Petroleum Engineers; 2010
- [73] Roussennac BD, Toschi C. Brightwater trial in Salema field (Campos basin, Brazil). In: SPE EUROPEC/EAGE Annual Conference and Exhibition, SPE-131299-MS. Society of Petroleum Engineers; 2010
- [74] Liu Y, Bai B, Shuler PJ. Application and development of chemical-based conformance control treatments in China oilfields. In: SPE/DOE Symposium on Improved Oil Recovery, SPE-99641-MS. Society of Petroleum Engineers; 2006

- [75] Aalaie J, Vasheghani-Farahani E, Rahmatpour A, Semsarzadeh MA. Effect of montmorillonite on gelation and swelling behavior of sulfonated polyacrylamide nanocomposite hydrogels in electrolyte solutions. *European Polymer Journal*. 2008;**44**:2024-2031
- [76] Bai B, Wei M, Liu Y. Field and lab experience with a successful preformed particle gel conformance control technology. In: *SPE Production and Operations Symposium*, SPE-164511-MS. Society of Petroleum Engineers; 2013
- [77] Al-Anazi H, Sharma M. Use of a pH sensitive polymer for conformance control. In: *International Symposium and Exhibition on Formation Damage Control*. Society of Petroleum Engineers; 2002
- [78] Lalehrokh F, Bryant S. Application of pH-triggered polymers for deep conformance control in fractured reservoirs. In: *SPE Annual Technical Conference and Exhibition*, SPE-124773-MS. Society of Petroleum Engineers; 2009
- [79] Tessarolli FGC, Queirós YGC, Mansur CRE. Evaluation of pH-sensitive hydrogels to control the permeability anisotropy of oil reservoirs. *Journal of Applied Polymer Science*. 2014;**131**(17)
- [80] Al-Muntasheri GA, Hussein IA, Nasr-El-Din HA, Amin MB. Viscoelastic properties of a high temperature cross-linked water shut-off polymeric gel. *Journal of Petroleum Science and Engineering*. 2007;**55**(1):56-66
- [81] Rousseau D, Chauveteau G, Renard M, Tabary R, Zaitoun A, Mallo P, et al. Rheology and transport in porous media of new water shutoff/conformance control microgels. In: *SPE International Symposium on Oilfield Chemistry*, SPE-93254-MS. Society of Petroleum Engineers; 2005
- [82] ElKarsani KSM, Al-Muntasheri GA, Sultan AS, Hussein IA. Gelation of a water-shut-off gel at high pressure and high temperature: Rheological investigation. *SPE J SPE-173185-PA*; 2014
- [83] Martin FD. Mechanical degradation of polyacrylamide solutions in core plugs from several carbonate reservoirs. *SPE Formation Evaluation*. 1986;**1**(02):139-150
- [84] Diaz I, Nava T, Deolarte C, Castillo O, Vasquez J, Cancino V, et al. Successfully controlling unwanted gas production in a highly naturally fractured carbonate reservoir. In: *SPE Western Venezuela Section South American Oil and Gas Congress*, SPE-163085-MS. Society of Petroleum Engineers; 2011
- [85] Stalker R, Graham GM, Oliphant D, Smillie M. Potential application of viscosified treatments for improved bullhead scale inhibitor placement in long horizontal wells-a theoretical and laboratory examination. In: *SPE International Symposium on Oilfield Scale*. Society of Petroleum Engineers; 2004
- [86] Vega I, Morris W, Robles J, Peacock H, Marin A. Water shut-off polymer systems: Design and efficiency evaluation based on experimental studies. In: *SPE Improved Oil Recovery Symposium*, SPE-129940-MS; 2010

