

A comprehensive review of *in situ* polymer hydrogels for conformance control of oil reservoirs

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Abstract. In fractured reservoirs, fluids injected Enhanced Oil Recovery (EOR) are channeled through the fracture zones and travel through highly permeable regions, failing to displace part of the oil, and decreasing oil recovery efficiency. To solve these problems, the conformance control technique is now widely used, as it allows the reservoir to be swept totally, similar to the ideal condition. In this context, polyacrylamide-based polymer gel systems can be used to block the high-permeability regions of the rock matrix, forming *in situ* hydrogels that block the rock pores, avoiding the channeling of the fluids, and increasing the oil production. These polyacrylamide-based hydrogels can be crosslinked by inorganic (metal ions) or organic substances, and various systems are used for conformance control. Due to the greater stability of the bond formed between the polymer and the organic crosslinker, these systems are now used in higher temperature reservoirs. In order to produce hydrogels with higher resistance to severe salinity and temperature conditions, nanoparticles are applied to form systems with good mechanical resistance, and high thermal stability. These have presented promising results for conformance control.

1 Introduction

Oil production is crucial for the global economy and its demand tends to increase by 1.5% per year (El-Hoshoudy *et al.*, 2017). There are a variety of technologies to facilitate the extension of the field life, such as advanced reservoir characterization, artificial lift optimization, conformance control, and various enhanced recovery schemes (Ali, 2010). Conformance control is any process by which the sweeping of a reservoir is spread more evenly, approaching the ideal condition of a perfectly conforming drive mechanism, minimizing water production (Bai *et al.*, 2015a).

In fractured reservoirs, injected fluids have a strong tendency to traverse regions of higher permeability, failing to displace some of the oil that could otherwise be recovered, thereby decreasing sweep efficiency (Chung *et al.*, 2011; Sheng, 2010). Another problem that occurs in mature fields is the large amount of produced water, which results in higher costs for oil separation processes, equipment corrosion, premature well abandonment, and environmental concerns related to the disposal of this water, among others (Al-Muntasheri, 2012; Imqam and Bai, 2015).

There are several types of water control treatments. The standouts are conventional zone-blocking water shut-off treatment and Relative Permeability Modifier Treatment (RPMT) (Alfarge *et al.*, 2018). The first treatment involves blocking the entire flow in a completely water-producing zone or stratum of the reservoir. The water shut-off material is normally a strongly crosslinked polymer gel, often referred to as a “blocking gel” (Cai and Huang, 2001). The second treatment includes selectively reducing the water while allowing the oil to flow freely or with minimal reduction. The material used in this operation is normally a polymer with low level of crosslinking (Al-Nakhli *et al.*, 2013).

Polymer hydrogels can be used as blocking gels, changing rock characteristics, and displacement mechanism, improving sweep efficiency, and consequently leading to a higher oil recovery rate (Lakatos and Lakatos-Szabó, 2008). These systems are injected in the reservoir formation from an injection well or a producing well, typically with 5–15 ft. (1.5–4.5 m) radial penetration (Powell *et al.*, 2004). The goal is to make the gel flow to the most permeable zones, sealing them by forming an impermeable blockage of the pores of the fractured rock. Through this process, water production can be decreased and oil production increased (Al-Muntasheri, 2012; Goudarzi *et al.*, 2015; Liu *et al.*, 2010). The polymer gel systems used for this type

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of treatment are usually composed of a polymer and inorganic or organic crosslinking agent, and are divided into two categories: *in situ* gels and Preformed Particle Gels (PPGs) (Lenji *et al.*, 2018). In this method, *in situ* gels are injected into the reservoir to form a 3D gel network structure, under reservoir conditions (temperature, salinity, and pH) so as to efficiently block water currents and reduce permeability (Seright, 1991; Sydansk and Moore, 1992). PPGs, however, undergo crosslinking before injection into the reservoir, forming gel under surface conditions, and being injected as preformed particles. *In situ* gel systems are less expensive, so they are the most widely used for conformance control (Goudarzi *et al.*, 2015; Imqam and Bai, 2015). The focus of this literature survey is the use of polymer hydrogels for water control treatment of oil reservoirs as “blocking gels” for *in situ* application.

2 Polymer gel systems for conformance control

In order to remedy conformance problems in reservoirs with high heterogeneity, characterized by fractured regions, and higher permeability zones, polymer gel systems can be used because of their easy pumping, low cost and ability to penetrate and change the reservoir permeability profile, leading to higher oil production (El-Karsani *et al.*, 2014a; Ma *et al.*, 2017; Tongwa and Baojun, 2015).

These systems are composed of a water-soluble polymer and crosslinking agent and were initially developed for *in situ* hydrogel formation (El-Karsani *et al.*, 2014a). When injected, the gelling process occurs inside the pores of the reservoir rock, generating a three-dimensional structure called hydrogel. The hydrogel acts as an impermeable physical barrier to water flow. By sealing the areas of greatest permeability, the injected fluids are forced to move to regions of low permeability, zones with large amounts of non-swept oil. This increases oil recovery (El-Karsani *et al.*, 2014a; Tongwa and Baojun, 2015; Zhu *et al.*, 2017a). This mechanism of blocking and changing the reservoir permeability profile is depicted in Figure 1.

The hydrogels have viscoelastic properties and their three-dimensional structure is formed by crosslinks that can involve van der Waals interactions, physical interlacing, ionic complexation, covalent bonding or hydrogen bonding, depending on the type of polymer, and the crosslinking agent used (Shibayama and Tanaka, 1993). Thus, the hydrogel does not dissolve in the porous medium and the transition time of the injected solution to the hydrogel (the three-dimensional structure formed), as well as its viscoelastic properties, strongly depend on the conditions of the petroleum reservoir, and the concentrations of the system's components (El-Karsani *et al.*, 2014b; Yavari-Gohar *et al.*, 2010; Zhu *et al.*, 2017a).

Oil reservoir conditions such as temperature, salinity, hardness, and pH of the formation water, rock fracturing pressure, permeability of the target zone, and the lithology of reservoir formation are important for the development of hydrogels (Manrique *et al.*, 2012; Zhu *et al.*, 2018). According to Tessarolli *et al.* (2014), polymer hydrogels need to

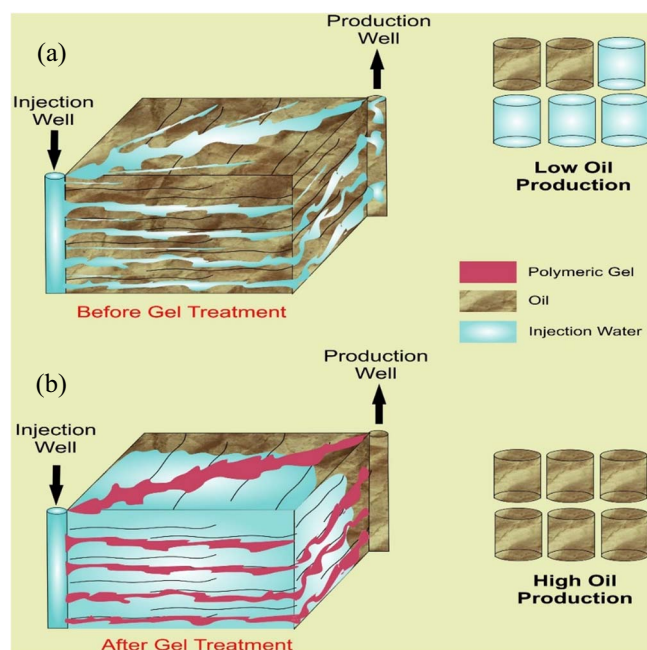


Fig. 1. Mechanism of action of the blocking gels, where: (a) the injected fluid flows preferentially through zones of greater permeability, reducing oil production and (b) formation of polymer gel preferentially in the thief zones of the reservoir, displacing the injected water to regions with lower permeability and increasing oil production.

have: (i) good injectivity (adequate intrinsic viscosity); (ii) low adsorption of their components in the porous medium and good propagation; and (iii) programmable gelation time.

To verify the applicability of hydrogel in conformance control, it is important to evaluate the gelling behaviors, such as:

- Gelation time – determines the length of time and depth that the system will reach when forming the impermeable barrier in the rock-reservoir.
- Gel strength and stability – indicate the performance of the hydrogel as a blocking agent.

These behaviors strongly depend on the type of polymer (molecular weight and degree of hydrolysis), polymer and crosslinking concentration and crosslinking agent type.

In general, polymer hydrogels should have a minimum gelation time of 2 h to ensure that the gel does not form during fluid injection. However, when the system is applied in regions far from the destination site, the minimum time passes to weeks or even months. The hydrogel formed must have thermal and chemical stability to withstand, under tank conditions, a minimum aging time of 6 months (Bai *et al.*, 2015b; Dang *et al.*, 2014; Johnson *et al.*, 2010; Zhang *et al.*, 2017).

Several *in situ* gel systems are being developed for the oil industry, such as gels based on synthetic polymers and

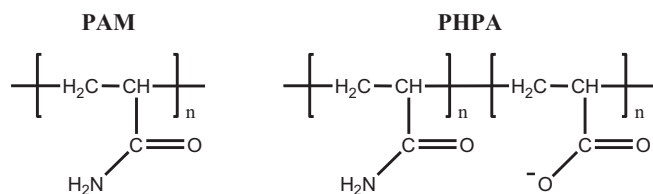


Fig. 2. Structure of polymers: (a) Polyacrylamide (PAM) and (b) Partially Hydrolyzed Polyacrylamide (PHPA).

polysaccharides (biopolymers) like xanthan gum, cellulose, starch, and lignin, among others (Bai *et al.*, 2015a). However, the costs to obtain the raw material and process biopolymers are very high, which often makes their use unfeasible. Thus, the use of synthetic polymers stands out, and the most prevalent are Polyacrylamide (PAM)-based gels (Bai *et al.*, 2015a; Jia *et al.*, 2012).

Polyacrylamide (Fig. 2a) is a water-soluble and electrically neutral polymer formed by a carbon chain with suspended amide groups. When exposed to high temperature or a small amount of alkaline solution, it undergoes thermal or basic hydrolysis, respectively, where amide groups are converted into anionic carboxylates groups, generating Partially Hydrolyzed Polyacrylamide (PHPA) (Fig. 2b). Thus, it forms a copolymer of acrylamide and acrylic acid (Ma *et al.*, 2015; Tongwa *et al.*, 2012).

The chemical properties and the ability to form viscous systems depend mainly on the molecular weight, degree of hydrolysis, and chemical composition of the polymer. For the preparation of gel systems, polyacrylamide has a high molecular weight, and in most cases a hydrolysis degree between 10% and 35% (Wever *et al.*, 2011). With the increase in the hydrolysis degree, the main chain of the polymer presents stronger electrostatic charges, which generate elongation of the polymeric chain in water due to electric repulsion, causing an increase in the viscosity of the system. However, a very high degree of hydrolysis can cause greater sensitivity to the salinity of the medium (Wever *et al.*, 2011).

Polyacrylamide hydrogels are sensitive to divalent ions and temperature. In brines with high concentrations of divalent cations, such as Mg^{2+} and Ca^{2+} , these cations interact with PHPA carboxylate anions, resulting in polymer precipitation. Thus, the possibility of precipitation with divalent ions increases with the use of polyacrylamide with a higher degree of hydrolysis (Reichenbach-Klinke *et al.*, 2011; Thomas *et al.*, 2012).

According to Ma *et al.* (2015), gels produced with polyacrylamide can be used for the treatment of reservoirs with temperatures below 90 °C. At higher temperatures, the thermal hydrolysis of the amide polyacrylamide groups accelerates, causing gel syneresis, which consists of the shrinking of the gel volume, and consequent expulsion of the water from the structure due to the increased density of crosslinks (Guan *et al.*, 2014).

Aiming to improve the thermal stability and salinity resistance of these gels, some polymers have been developed from the copolymerization of PAM with comonomers, such as Vinylpyrrolidone (VP), 2-Acrylamid-Methylpropane

Sulfonic (AMPS) acid or its Sodium 2-Acrylamid-Methylpropane Sulfonate (Na-AMPS) salt, and Tert-Butyl Acrylate (tBA) (El-Karsani *et al.*, 2014a; Thomas *et al.*, 2012; Zhang *et al.*, 2017).

In general, these groups in PAM's polymeric chain exert a shielding effect, protecting the amide groups from thermal hydrolysis, reducing their conversion into carboxylic group, and thus increasing the thermal stability of the polymer. In addition, this makes it more resistant to salinity, because the number of carboxylate anions in the polymer structure decreases, making the interaction of these anions with divalent cations less pronounced (Thomas *et al.*, 2012; Zhang *et al.*, 2017; Zhu *et al.*, 2017a).

Polymer gel systems based on polyacrylamide can be formed from the use of organic crosslinking systems, where their formation occurs by covalent bonds, or inorganic crosslinking systems, crosslinked by ionic bonds (Jia *et al.*, 2012). The following sections address the main types of crosslinking agents used for the formation of gel systems applied for conformance control.

2.1 Acrylamide-based polymers with inorganic crosslinking systems

The most widely used inorganic crosslinkers are multivalent metal ions such as Cr^{3+} , Al^{3+} , Zr^{4+} , Fe^{3+} , and Ti^{3+} to form gel systems with polyacrylamide-based polymers. The polyacrylamides used for *in situ* gel systems are all partially hydrolyzed to carry a negative charge. The crosslinking mechanism of these gels is the ionic bond between the negative charges of the polymer carboxylate groups and the multivalent cations (Jia *et al.*, 2010; Zhu *et al.*, 2017b).

These metal ions can be found in the form of soluble chemical complexes in solution or as simple inorganic ions. The rate and extent of the reaction depends heavily on the binder structure of the crosslinking agent. Cr(III) is the most used metallic ion for the formation of these systems, but its oxidation can generate Cr(VI), which is highly carcinogenic and thus has a great disadvantage in relation to other inorganic crosslinkers (Albonico *et al.*, 1993; Jia *et al.*, 2012; Vargas-Vasquez and Romero-Zerón, 2008).

The first polymer gel system formed for conformance control was produced by Routson and Caldwell (1972) from PHPA injection with a diluted Cr(III) hydroxide solution. However, a lack of control of the gelation time was observed. In the early 1980s (American Petroleum Institute, 1982), a study was performed of PHPA crosslinked with aluminum sulfate and a close relationship was observed between these systems and the pH conditions, because when the polymer was mixed with aluminum sulfate under acid conditions in surface installations, the mixture did not form a gel immediately and could be successfully injected into the reservoir, but when the fluids penetrated the formation, the pH increased very fast, causing gelling to occur in an uncontrolled manner, making its application impossible in areas far from the injection well.

In order to improve the gelation time and ensure the formation of the gel in the desired region, several authors have conducted studies using multivalent ions in the form of complexes, such as citrate, acetate, malonate, propionate,

tartrate, and metallic ion glycolate (Albonico *et al.*, 1993; Bai *et al.*, 2015a; Ghazalli and Willhite, 1985; Kedir *et al.*, 2014; Moradi-Araghi *et al.*, 1988; Needham *et al.*, 1974; Romero-Zerón *et al.*, 2008).

Needham *et al.* (1974), Ghazalli and Willhite (1985), and Moradi-Araghi *et al.* (1988) all carried out studies of gel systems with PHPA/Al(III) citrate. The authors observed that the citrate ions acted as a protector of the Al^{3+} ions, allowing the system to be injected into the reservoir with the polymeric solution and to perform crosslinking. Without forming a complex with citrate, aluminum could be hydrolyzed to an aluminum hydroxide precipitate, making the metal ions unavailable for crosslinking, thus not forming gels. In addition, it was found that the pH range between 6 and 7 is ideal for the gelling of these systems.

Systems based on PHPA/Cr(III) propionate were studied and patented by Mumallah and Shioyama (1987), found to be effective for the treatment of zones with higher permeability near or far from the injection well and resistant to environments with higher salinity.

Sydansk (1988) established and patented a new polymer gel system based on PHPA/Cr(III) acetate. This system achieved great prominence in oil fields. The acetate group has a very similar structure to the carboxylate group present in PHPA. Thus, the Cr^{3+} ions are attracted both by the negative charges of the PHPA carboxylate group and the acetate binder, delaying the formation of crosslinks and making the gelation time programmable. In addition, these systems had as advantages their resistance to reservoirs with high temperatures (124 °C or higher) and insensitivity in the pH range between 2 and 12.5. As a disadvantage, these systems still had low gelation time, precluding their application in areas with greater distance from the injection wells (Sydansk, 1988).

Since then, these Cr(III) systems have been applied, for example, in the Big Horn Basin in Wyoming, where an increase of 1 200 000 barrels of oil from stock tanks was observed due to the injection treatment with PHPA/Cr(III) acetate in the wells from 1989 to 1992 (Southwell and Posey, 1994).

Fletcher *et al.* (1992) studied the ability of systems formed by PHPA/Al(III) citrate to withstand environments with formation water having high salt content (30 000 TDS).

Albonico *et al.* (1993) evaluated the delaying effect of Cr(III) complexes with glycolate, malonate, and salicylate on PAM-AMPS copolymers at 120 °C. A positive effect was observed, where the gelation time was 12–33 times longer than that gelation time using acetate. It was also found that the delay in gelling is highly dependent on the concentration of the ligand present in the solution and has a direct relationship, which can be explained by the competition of the Cr^{3+} ions for crosslinking in interacting with the ligand of the complex (Albonico *et al.*, 1993).

Stavland and Jonsbraten (1996) conducted studies of the gelation time with Al(III) citrate crosslinker at 90 °C and found that the gelation time varied between 3 and 30 days, with a tendency to increase at higher pH values and decrease with higher aluminum concentration.

Cai and Huang (2001) evaluated systems with 400 mg L⁻¹ PHPA and different concentrations of Ti(IV) tartrate crosslinker at 50 °C. The authors observed that up to 250 mg L⁻¹ of the crosslinker, the gelation time was effective but above this concentration a polynuclear titanium complex formed, causing less efficient crosslinking, and reducing the gel strength. They also found that the rate of gelling increased with the highest content of sodium chloride in the formation water and that the pH range for this was between 4.9 and 6.6. Thus, Ti(IV) tartrate can be applied in reservoirs with high salinity, pH values close to neutral and moderate temperatures.

Grattoni *et al.* (2001), Seright *et al.* (2003), Cheng *et al.* (2005), Vargas-Vasquez and Romero-Zerón (2008), and Romero-Zerón *et al.* (2008) conducted studies with gel systems of PHPA/Cr(III) acetate. Although the PHPA/Cr(III) acetate gel system has been successful in oil fields, some inherent problems have occurred. Pre-gel aggregates were formed even before a gel network was established. Rock reservoirs filtered them out and retained them according to their size or molecular weight, causing problems in conformance control treatment. Thus, it became necessary to carry out further studies to optimize this process using the components of this system.

Koohi *et al.* (2010) prepared hydrogels with Cr(III) acetate and AM-AMPS copolymer. The minimum concentration of polymer to form a gel at 90 °C was 5500 ppm (0.55% mass). Parameters such as gelling rate, viscosity and gel strength increased with the use of higher polymer concentrations and crosslinking/polymer ratios, due to the greater availability of carboxylate clusters to interact with Cr^{3+} .

Dang *et al.* (2014) conducted studies with PHPA having low molecular weight (Alcoflood 254S) at a concentration of 20 000 mg L⁻¹ and Cr(III) acetate, with a crosslinking/polymer ratio (*R*) equal to 1/40, and analyzed the influence of temperature on gelation time. Gelation times of 24 h were observed at 40 °C, 4.5 h at 55 °C, and much shorter times at temperatures of 60–75 °C. In other words, higher temperatures increased the viscosity of the systems, indicating faster gelling. In addition, they studied the gelling behavior in relation to the molecular weight of the polymer used, comparing Alcoflood 254S and PHPA of average molecular weight, commercially known as Alcoflood 955. The influence of molecular weight, where the higher mass polymer formed gel more quickly, was attributed to the higher number of carboxylate clusters to react with Cr^{3+} .

Kedir *et al.* (2014) developed hydrogels formed of 600 mg L⁻¹ of PHPA with hydrolysis degree of 25–30% and 20 mg L⁻¹ of Al(III) citrate (AlCit) and studied the influence of pH on crosslinking of the systems. They found that these systems were strongly affected by pH variations, that AlCit was more reactive at almost neutral pH and therefore crosslinking reactions should preferably be performed under these conditions.

Moghagam *et al.* (2014) formed systems with PA-AMPS with 25% sulfonation, known commercially as AN125, using chromium triacetate as crosslinking agent, sodium lactate as retardant, Sodium Montmorillonite (Na-MMT), and brine (sodium chloride – NaCl, calcium

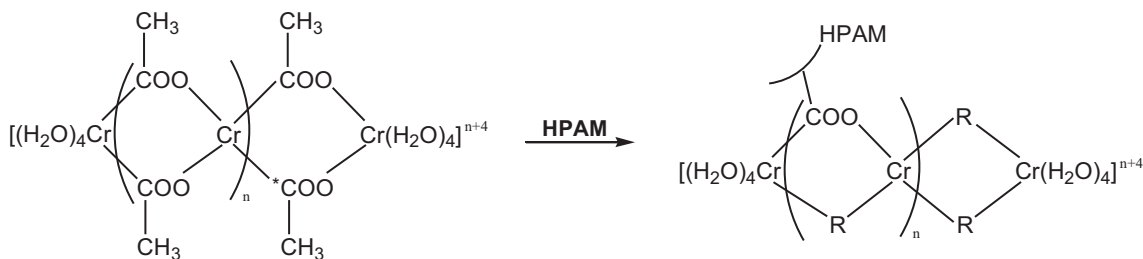


Fig. 3. PHPA/Cr(III) acetate crosslinking mechanism.

chloride – CaCl_2 , potassium chloride – KCl and magnesium chloride – MgCl_2) and carried out a two-level factorial experiment design (multivariate statistical analysis) to find the parameter that most influenced the gelation time of these systems.

The factors evaluated in this design were: NaCl concentration ($15\,000\text{ mg L}^{-1}$ or 0 mg L^{-1}), CaCl_2 ($15\,000\text{ mg L}^{-1}$ or 0 mg L^{-1}), KCl ($15\,000\text{ mg L}^{-1}$ or 0 mg L^{-1}), and MgCl_2 ($15\,000\text{ mg L}^{-1}$ or 0 mg L^{-1}), temperature ($90\text{ }^\circ\text{C}$ or $60\text{ }^\circ\text{C}$), pH (11 or 3), addition of sodium lactate (1% m/m or 0), and Na-MMT (1% m/m or 0). Gelation time increased with the use of a retardant and addition of MgCl_2 , while it decreased with the increase in temperature, pH, addition of Na-MMT and other salts. Temperature had the greatest effect on the gelation time of these systems (Moghagam *et al.*, 2014).

Zhang *et al.* (2015a) studied the crosslinking mechanism between PHPA and Cr(III) acetate and observed that the process occurs in two types of reactions. The first reaction consists of intramolecular crosslinking, where Cr^{3+} interacts with carboxylate groups of a molecule of PHPA; and the second reaction consists of intermolecular crosslinking, where Cr^{3+} ions interact with carboxylate groups of different molecules of PHPA, generating the three-dimensional structure of the gel and causing an increase in system viscosity.

Figure 3 shows schematically the crosslinking mechanism between PHPA/Cr(III) acetate, where the metal ions cease to interact with the acetate binder (R) and start to form ionic bonds with the PHPA carboxylates, generating three-dimensional gel structures.

The influence of the hydrolysis degree of PHPA on the occurrence of syneresis in PHPA/Cr(III) hydrogels was studied by Zhang *et al.* (2015b). For this, hydrogels were prepared with three PHPA samples of the same molecular weight and with 20%, 30%, and 39% hydrolysis degree. As polymer hydrolysis increased, more carboxylates were present in the PHPA structure, allowing greater reticulation density of the hydrogel, so the water present in the three-dimensional structure was expelled more easily, generating syneresis, and destabilization of the system. Thus, a higher hydrolysis degree of PHPA provides a higher rate of syneresis.

Sun *et al.* (2016) developed a system with delayed crosslinker formed by polyacrylamide, thiourea as a stabilizer, sodium carbonate to control the hydrolysis degree, and Cr(III) acetate. The hydrolysis degree of PAM was controlled at 0.01% and 0.001%, and the polymer and

crosslinker concentrations were 5000 mg L^{-1} and 500 mg L^{-1} , respectively. At $65\text{ }^\circ\text{C}$, the gelation time increased from 8 to 30 days with the decrease of the hydrolysis degree, giving the system enough time to flow into deeper areas. Thus, this system showed promise for application in locations further from the injection wells (Sun *et al.*, 2016).

Alsheri *et al.* (2019) studied a gel system formed by sulfonated polyacrylamide and Cr(III) acetate and evaluated the system's efficiency to seal fracture zones in carbonate rock plugs under high-salinity and high-temperature conditions. The injected gel system was formed by 4000 ppm polymer and 100 ppm Cr(III) and the tests were performed at $95\text{ }^\circ\text{C}$ in different rock plugs. They verified that the conformance control treatment with this hydrogel was promising, because it provided improvements in the oil recovery factor between 12.0% and 37.6%.

In general, the gelation time of systems composed of polyacrylamide crosslinked by metal ions depends on the polymer and crosslinker concentration, hydrolysis degree of the polymer, temperature, pH, and salinity. The summary of activities performed with acrylamide-based polymers and inorganic crosslinkers is presented in Table 1. Although many studies have been published, these inorganically crosslinked systems have limitations for application to conformance control of reservoirs with higher temperature and salinity conditions (Bai *et al.*, 2015a; Zhu *et al.*, 2017b). Thus, systems formed by organic crosslinkers have been and are being developed to try to overcome the limitations of crosslinking by multivalent metal ions.

2.2 Acrylamide-based polymers with organically crosslinked systems

Gel systems based on polyacrylamide can be formed by crosslinking with organic compounds such as phenol-formaldehyde, resorcinol-formaldehyde, hydroquinone – hexamethylenetetramine, N,N' -methylenebisacrylamide Polyethyleneimine (PEI), among others. In these gels, the crosslinks generating the three-dimensional structures are formed by covalent bonds between the amide groups of the polymer and the functional groups of the organic crosslinking agents. Due to the greater stability that covalent bonds give to gels, these systems are promising for application in reservoirs with higher salinity and temperature, and thus, have advantages over metal ion crosslinked systems (Al-Muntasheri *et al.*, 2008a, b; Chung *et al.*, 2011;

Table 1. Summary of activities performed with acrylamide-based polymers and inorganic crosslinkers.

Year	Activity	Authors
1972	Developed the first gel system – PHPA with a diluted Cr (III) hydroxide solution	Routson and Caldwell
1982	Studied gel system of PHPA crosslinked with aluminum sulfate and evaluated pH influence	<i>American Petroleum Institute</i>
1974, 1985, and 1988	Prepared gel systems with PHPA/Al(III) citrate and evaluated the effect of citrate ions	Needham <i>et al.</i> Ghazalli and Willhite Moradi-Araghi <i>et al.</i>
1987	Analyzed systems based on PHPA/Cr(III) propionate	Mumallah and Shioyama
1988	Patented a new polymer gel system based on PHPA/Cr(III) acetate	Sydansk
1992	Evaluated the resistance of systems formed by PHPA/Al(III) citrate	Fletcher <i>et al.</i>
1993	Evaluated the delaying effect of Cr(III) complexes with glycolate, malonate and salicylate on PAM–AMPS	Albonico <i>et al.</i>
1994	Applied Cr(III) systems in the Big Horn Basin in Wyoming	Southwell and Posey
1996	Studied the effects of Al(III) citrate on the gelation time	Stavland and Jonsbraten
2001	Developed gel systems with PHPA and Ti(IV) tartrate	Cai and Huang
2001, 2003, 2005, 2008, and 2008	Conducted studies with gel systems of PHPA/Cr(III) acetate	Grattoni <i>et al.</i> Seright <i>et al.</i> Cheng <i>et al.</i> Vargas-Vasquez and Romero-Zerón Romero-Zerón <i>et al.</i>
2010	Prepared hydrogels with Cr(III) acetate and PAM–AMPS	Koohi <i>et al.</i>
2014	Evaluated the influence of molecular weight and temperature on PHPA/Cr(III) acetate systems	Dang <i>et al.</i>
2014	Developed hydrogels formed of PHPA and Al(III) citrate and evaluated the influence of pH	Kedir <i>et al.</i>
2014	Formed systems with PAM–AMPS, chromium triacetate and added sodium lactate as a retardant (to increase gelation time)	Moghagam <i>et al.</i>
2015a	Studied the influence crosslinking mechanism between PHPA and Cr(III) acetate	Zhang <i>et al.</i>
2015b	Studied the influence of the hydrolysis degree of PHPA on the syneresis in PHPA/Cr(III) hydrogels	Zhang <i>et al.</i>
2016	Developed a system with delayed crosslinking formed by PAM, thiourea, sodium carbonate and Cr(III) acetate	Sun <i>et al.</i>
2019	Evaluated the efficiency of sulfonated polyacrylamide and Cr(III) acetate systems	Alsheri <i>et al.</i>

Ghriga *et al.*, 2019; Yavari-Gohar *et al.*, 2010; Zhu *et al.*, 2017c).

These gels are called Organically Crosslinked Gels (OCGs) and for their formation, the polyacrylamide can be used in its homopolymer (PAM), partially hydrolyzed (PHPA) or copolymerized form, such as: PAM–NVP, PAM–AMPS or PAM–tBA. The viscoelastic properties of OCG, gelation time, thermal stability, and salinity resistance are determined by the composition of these systems (Bai *et al.*, 2015a; Chung *et al.*, 2011; Jayakumar and Lane, 2013).

The first gels formed by organic crosslinking agents were developed by Chang *et al.* (1984), who produced gel systems based on polyacrylamide crosslinked by resorcinol-formaldehyde and phenol-formaldehyde. After this study, Moradi-Araghi (1993), Bryant *et al.* (1997), Moradi-Araghi (2000), and other researchers developed phenol-formaldehyde crosslinked systems. The authors verified that the gelling mechanism was formed by the reaction product of phenol with formaldehyde and the amide groups of the polymer, observing the formation of stable gels. According Moradi-Araghi (1993), the gels produced with 1% w/v polymer in the formation water remained stable for 13 years at aging temperature of 121 °C.

Although these systems have been applied in several reservoir conformance treatments and have shown satisfactory results, this organic crosslinking agent is now less used due to the high toxicity of phenol, and mainly the carcinogenic characteristic of formaldehyde (Chung *et al.*, 2011; Moradi-Araghi, 2000).

Thus, researchers began to develop crosslinking systems composed of Hydroquinone (HQ) and Hexamethylenetetramine (HMTA) to replace phenol-formaldehyde and remedy the problems caused by its use. HMTA is a less toxic derivative of formaldehyde and the HQ in high concentrations is harmful to aquatic life. However, the crosslinking systems formed by these two components are less toxic than phenol-formaldehyde (Liu *et al.*, 2016; Sengupta *et al.*, 2012).

Hutchins *et al.* (1996) were the first to produce and report the application of polyacrylamide gels crosslinked with HQ–HMTA for use in high temperature reservoirs. These systems showed good gelling properties, with stability at 149 °C for 1 year and at 176.7 °C for 5 months. The authors considered them to be highly applicable for conformance control in high permeability areas. Dovan *et al.* (1997) also studied these systems and observed that the gels had a long gelation time and better thermal stability than those crosslinked by phenol-formaldehyde.

Sengupta *et al.* (2012) conducted studies of the properties of gels formed by polyacrylamide and hydroquinone–hexamethylenetetramine and verified the formation of gels with high mechanical resistance at 120 °C and that the ideal pH value for this was 9.5.

Yadav and Mahto (2013a, b) studied the gelling kinetics and rheological properties of gels formed by PHPA/HQ–HMTA. They observed that the rheological behavior varied over time, because the viscosity of the system became higher as the gelation time increased due to the formation of crosslinks, while this time decreased with the increase in gel concentration of HQ–HMTA.

Yadav and Mahto (2013c), Sengupta *et al.* (2014), and Liu *et al.* (2016) investigated the influence of polymer and crosslinking concentration, temperature, salinity and pH value on gelation time and gel strength in PAM/HQ–HMTA systems. According to Liu *et al.* (2016), the hydrogels formed by 6000 mg L⁻¹ PAM, and 6000 mg L⁻¹ HQ–HMTA showed high thermal stability and can be applied in reservoirs with temperatures up to 140 °C.

In a more recent study, Fang *et al.* (2017) developed gel systems with PHPA and HQ–HMTA with resistance to High Temperature and Salinity (HTHS) conditions. The authors observed that the gel strength increased and gelation time decreased for higher polymer and crosslinker concentration and higher temperature. They also found that these systems had good injectivity and flowed selectively to the zones of greater permeability.

In order to use organic crosslinkers considered to be environmentally friendly, Polyethyleneimine (PEI) is now used for polyacrylamide-based hydrogels, and it has been successfully applied in several oil fields, due to the formation of stable systems in a wide temperature range. This organic crosslinking agent has become the most widely used in the world during the last decade (Al-Muntasheri *et al.*, 2008b; Zhao *et al.*, 2011).

In general, the crosslinking mechanism of PEI with polyacrylamide and its derivatives occurs via a transamidation reaction. In this reaction, the imine nitrogen of PEI performs a nucleophilic attack on the amide carbonyl group of PAM, replacing a substitution of the amide group, forming covalent bonds between the crosslinks and the main polymer chain (Al-Muntasheri, 2012; Jia *et al.*, 2012; Zhao *et al.*, 2011). The mechanism of this reaction using PEI as a crosslinking agent can be seen in Figure 4.

The first system stable crosslinked by PEI was described by Hardy *et al.* (1999), who produced a gel system formed of acrylamide/butyl acrylate copolymer and polyethyleneimine (PAM–tBA/PEI). Hardy *et al.* (1998, 1999) also studied PAM–tBA/PEI gels, where the gelation kinetics of the system was observed along with the effect of pH variation on the crosslinking time, showing a slight increase at higher pH values. The excellent propagation and thermal stability of these systems were verified and thus began to be developed for commercial use.

Hardy *et al.* (1999) observed that the ester groups of the PAM–tBA copolymer may undergo hydrolysis or thermolysis according to pH and temperature conditions. At low pH, these groups hydrolyze forming PHPA and *t*-butyl alcohol. At high pH and temperature, the copolymer undergoes thermolysis, producing PHPA, and isobutene. In these cases, crosslinking occurs by nucleophilic attack of the imine nitrogen of the carbonyl carbon on the ester group. However, the crosslinking occurs only at temperatures below 100 °C and reaction times below 20 h.

Al-Muntasheri *et al.* (2007) investigated the viscoelastic properties of gels formed by PAM–tBA (3–7% w/v) and PEI with a molecular weight of 70 000 g/mol (0.3–1.2% w/v), in injection water, saline water of 5000 ppm TDS and distilled water at a temperature of 150 °C and aging for 30 days. An increase in elastic modulus (G') and a decrease in gelation time were observed for higher

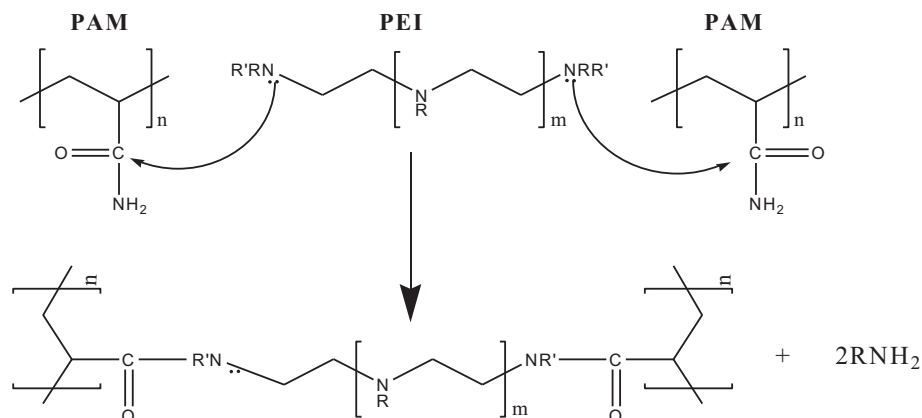


Fig. 4. PAM–PEI systems' crosslinking mechanism.

crosslinking and polymer concentrations, but for these same concentrations (7 wt% PAM–tBA and 1.2% PEI), syneresis was observed at 30 days, reducing G' values by 53%. They also observed that increasing salinity provided a longer gelation time and decreased elastic modulus.

Al-Muntasheri *et al.* (2008b) prepared PEI-crosslinked PAM hydrogels and studied gelling kinetics under High Temperature (100–140 °C) and Pressure (30 Bar) (HTHP) conditions, evaluating the effect of temperature, and salinity. For this purpose, gel systems were prepared with 7% mass of PAM and 0.3% PEI in distilled water, brine of 30 000 and 50 000 mg L⁻¹ TDS of NaCl. They observed that temperature is an extremely important factor for the gelling kinetics of PAM/PEI systems and its increase promoted a decrease in gelation time, with gelling time of 0.67 h for systems produced with water and times of 4.4 and 6.8 h for systems produced with 30 000 and 50 000 mg L⁻¹ NaCl, respectively. This indicates that the gelation time increases for systems with larger amounts of NaCl in brine, suggesting that this salt may be used as a delayed gelling agent in high temperature reservoirs.

Al-Muntasheri *et al.* (2009) performed a comparative study between the gelling process of PAM/PEI and PAM–tBA/PEI systems, using 7% mass of polymer and 1% mass of PEI, distilled water and aging at 120 °C. They observed that the gelation time of PAM/PEI (13.5 min) was shorter than that of PAM–tBA/PEI (28 min), indicating greater availability of reaction sites in PAM than in PAM–tBA. These systems were not suitable for application in reservoirs due to their fast gelation time, but this could be adjusted by reducing polymer and/or crosslinking concentrations.

Jia *et al.* (2010) investigated the influence of polymer concentration and molecular weight on the formation of PAM/PEI gels. Systems containing 0.5% to 1.5% by mass PAM (with weight-average molecular weights of 2000, 4000, and 8000 kg/mol) were prepared with 1% PEI, brine with 9000 mg L⁻¹ TDS at a temperature of 40 °C. They observed that with increasing polymer concentration, the number of crosslinking points in the polymer increased, raising the crosslinking rate and consequently reducing the gelation time. Regarding molecular weight, a slight decrease in gelation time and a small increase in gel strength

were considered for systems produced with greater molecular weight.

In another study, Jia *et al.* (2012) concluded that the main factors that influence gelling performance are polymer concentration, crosslinking concentration, PAM molecular weight, and Total Dissolved Salts (TDS) in the water used to prepare the systems.

Zhao *et al.* (2011) investigated the performance of PAM/PEI systems to seal fractured regions and found that the gel formed by 2% mass of PAM ($M_w = 8000$ kg/mol), 0.35% mass of PEI ($M_w = 20$ kg/mol) in brines of 5000 mg L⁻¹ TDS. This system was a promising blocking agent for use in fractured reservoirs with temperature of 65 °C, as it presented high mechanical performance and resisted the maximum pressure gradient of 1136.38 psi/ft in cores with fractures from 0.080 cm to 0.200 cm.

Jayakumar and Lane (2012) developed a delayed gelling system consisting of PAM and a mixture of PEI and dextran sulfate. They noted that the PEI was available for crosslinking with the polymers only when its interaction with dextran sulfate was interrupted, increasing the gelation time. However, this delaying agent is very expensive and its use on a commercial scale for reservoirs has become unfeasible.

Thus, Jayakumar and Lane (2013) replaced the use of dextran sulfate with 2-acrylamid-methylpropane sulfonic acid, since it is cheaper, easily available and widely used in oil fields, and studied the delayed gelling system formed by PAM–PEI–AMPS. They observed that PEI/AMPS was an effective crosslinking retardant agent because in systems containing 0.4% mass of crosslinked PAM with 0.4% PEI, the gelation time was 13 h but when crosslinked by 0.4% PEI:AMPS retardant system in the ratio of 2:1, this time increased to 120 h, showing the efficiency of the process. In addition, the decrease in the PEI:AMPS ratio promoted a longer delay of the gelling process.

El-Karsani *et al.* (2014b, c) prepared systems with 7% mass of PAM cross-linked by 0.3% PEI, in distilled water with the addition of 12 000 ppm of NaCl or NH₄Cl and in formation water with the same quantities and types of added salts in distilled water, and studied the effect of these different salts on gelling retardation and gel strength,

comparing the action of NaCl and NH_4Cl . They noted that both in distilled water and in formation water, the addition of salts promoted the delay of gel formation and a slight decrease in gel strength. The use of NH_4Cl caused this effect to occur more markedly than the addition of NaCl (El-Karsani *et al.*, 2014c).

According to Bai *et al.* (2015b), gel systems can also be prepared with Hydrophobically Associated Polyacrylamide (HAP), when it contains one or more hydrophilic groups and a small number of hydrophobic groups. Thus, the systems were prepared with 0.35% w/w HAP (12 000 kg/mol molecular weight) and 0.60% PEI (12 kg/mol) at 80 °C. This HAP/PEI system formed a gel with good stability and gelation time of 45 h, which could be delayed by the addition of CaCl_2 and NaCl or by lowering the temperature.

Hashmat *et al.* (2016) studied systems formed by PHPA with hydrolysis degree of 25–30% and molecular weight of 8000 kg/mol (commercially known as Flopaam 3330S) and an anionic copolymer based on polyacrylamide with the commercial name Alcomer 130 (A130), with molecular weight considered ultra-high compared to Flopaam 3330, with crosslinking by PEI. Thus, the systems were prepared with 3% 3330S polymer, 0.6%, 1.0% and 1.2% PEI, and 2% A130 polymer with the same amount of PEI. The thermal stability of these systems was studied at 100 °C for 28 days of aging.

According to the authors, it is essential to study the thermal stability of gels due to the polymer, which can undergo hydrolysis at high temperatures, resulting in the syneresis of the gel system, with a significant reduction in the gel volume. A thermally stable gel does not undergo syneresis, and consequently shows few signs of gel retraction. Thus, all systems prepared for that study with 3330S and A130 remained stable, with no significant retraction in volume, and formation of rigid and non-fluid gels (Hashmat *et al.*, 2016).

Zhang *et al.* (2017) produced a terpolymer formed by 2-acrylamide-2-tetradecyl ethyl sulfonic acid (AMC16S), Acrylamide (AM) and Acrylic Acid (AA), with temperature resistance of 100 °C, indicating that it might be suitable to form gels. This acrylamide-based terpolymer was crosslinked by PEI and its properties were studied to apply this gel in conformance control of high temperature reservoirs. According to the authors, the gel systems formed by 3000 mg L^{-1} terpolymer and 2000 mg L^{-1} PEI slowed gelation time, and gel strength was affected by salinity, pH and temperature conditions. In addition, this system showed good shear resistance, ensuring that the gel system was not destroyed during transport through the porous formation and had thermal stability for a long period. Thus, these systems can be used as blocking gels in deeper regions of the reservoir.

Ma *et al.* (2017) developed systems composed of PHPA, PEI and Silica Nanoparticles (SNP) in order to improve the performance of gels. Systems were prepared with 1% w/w of PHPA, 0.2% w/w of PEI and 0.63% w/w of SNP with diameters of 9–12 nm in formation water with 53 200 mg L^{-1} TDS. They performed a comparative study of PHPA/PEI and PHPA/PEI–SNP gels. The gelation time of the PHPA/PEI system was approximately 30 h and with the addition of SNP this time was extended to

132 h. The strength of the PHPA/PEI–SNP gel remained the same as that of the PHPA/PEI system and showed excellent thermal stability at 85 °C for 28 days, without presenting syneresis, unlike the PHPA/PEI system, which presented dehydration after aging for 17 days.

Chen *et al.* (2018) developed PAM–PEI systems reinforced with nanosilica having particle size of 28.6 nm, with varying nanoparticle concentrations (0%, 0.1%, 0.3%, and 1% by mass), to verify the reinforcement and stabilizing power. They observed that the increased in nanosilica concentration provided higher gel strength, shorter gelation time and greater stability of the systems. Hydrogels without nanosilica remained stable (without syneresis) at 130 °C for 18 days, increasing to 35 days with 0.1%, 65 days with 0.3% and 180 days with 1% nanosilica. When comparing the microstructure of nanocomposite hydrogels with the common one, a denser and stronger three-dimensional network was observed. Thus, it can be inferred that the silanol group of the nanoparticle formed crosslinks with the hydrogen of the amide group of PAM by hydrogen bonds, providing reinforcement in the hydrogel structure.

Lashari *et al.* (2018) also studied the action of nanosilica as a reinforcement filler in systems formed by polymer based on polyacrylamide crosslinked by resorcinol-hexamethylenetetramine, at temperature of 100 °C and salinity 51 984 ppm TDS. They observed improved thermal stability (no syneresis) for about 90 days and increased gel strength.

Jia and Chen (2018) developed gel systems with multiple crosslinking of PHPA, Cr(III) acetate, and polyethyleneimine (Cr^{3+} –PEI–PHPA), in order to study the gelling behavior and improve the properties. For the crosslinked systems with Cr^{3+} , they noted the formation of a weak gel (“pre linked gel”), which showed good pumping capacity and reduced adsorption of polymer in the plugs, ensuring good gelling performance. When increasing the temperature during the pumping process, second-stage crosslinking took place, with the formation of covalent bonds with PEI, generating high gel strength, applicable for conformance control.

Adewunmi *et al.* (2018) used Coal Fly Ash (CFA) as an additive to improve the properties of hydrogels. This material is obtained from burning coal and consists mainly of alumina and silica. The authors prepared PHPA–PEI and PHPA–PEI–CFA hydrogels, with nanofiller concentrations of 0.5%, 1% and 2% w/w. From rheological analyses they found that PAM–PEI–CFA hydrogels showed more elastic behavior than PAM–PEI hydrogels, indicating the CFA’s dispersion and strengthening effect. This reinforcement was stronger with increasing load content. In addition, the nanocomposite hydrogel with 2% CFA was subjected to tests to simulate the action as sealant of fracture zones in reservoir rocks to evaluate the effectiveness of gel blocking at a temperature of 90 °C. The result showed considerable sealing power.

Zhu *et al.* (2019) studied the effects of polymer and crosslinker concentration, PEI molecular weight and salinity on the gelation performance of hydrogels formed by terpolymer (AM–AMPS–NVP) and crosslinked by polyethyleneimine at 150 °C. They found that polymer

Table 2. Summary of activities performed with acrylamide-based polymers and organic crosslinkers.

Year	Activity	Authors
1984	Formation of the first gels by organic crosslinking – PAM/resorcinol-formaldehyde and PAM/phenol-formaldehyde	Chang <i>et al.</i>
1993	Developed phenol-formaldehyde crosslinked systems	Moradi-Araghi
1996	Produced and reported the application of PAM gels crosslinked with HQ–HMTA for use in high-temperature reservoirs	Hutchins <i>et al.</i>
1997	Observed a long gelation time and thermal stability of PAM/HQ–HMTA systems	Dovan <i>et al.</i>
1997	Developed phenol-formaldehyde systems	Bryant <i>et al.</i>
1998 and 1999	Produced the first stable crosslinked by PEI	Hardy <i>et al.</i>
2000	Developed phenol-formaldehyde crosslinked systems	Moradi-Araghi
2007	Investigated the viscoelastic properties of gels formed by PAM–tBA and PEI	Al-Muntasheri <i>et al.</i>
2008b	Studied gelling kinetics of PAM/PEI systems under HTHP conditions	Al-Muntasheri <i>et al.</i>
2009	Developed a comparative study between PAM/PEI and PAM–tBA/PEI	Al-Muntasheri <i>et al.</i>
2010	Investigated the influence of polymer concentration and molecular weight on PHPA/PEI hydrogels	Jia <i>et al.</i>
2011	Evaluated the performance of PHPA/PEI systems	Zhao <i>et al.</i>
2012	Conducted studies of the properties of PAM/HQ–HMTA hydrogels	Sengupta <i>et al.</i>
2012	Concluded that several factors influence the gelling performance of PHPA/PEI systems	Jia <i>et al.</i>
2012	Developed a delayed gel system consisting of PHPA, PEI, and dextran sulfate	Jayakumar and Lane
2013a, b	Studied the gelling kinetics of gels formed by PHPA/HQ–HMTA	Yadav and Mahto
2013	Developed gel systems with PHPA, PEI and AMPS	Jayakumar and Lane
2014	Investigated the influence of several factors on PAM/HQ–HMTA systems	Sengupta <i>et al.</i>
2014b, c	Evaluated the action of NaCl and NH ₄ Cl in PAM/PEI systems	El-Karsani <i>et al.</i>
2015b	Prepared systems with hydrophobically associated polyacrylamide and PEI	Bai <i>et al.</i>
2016	Investigated the influence of several factors on PAM/HQ–HMTA systems	Liu <i>et al.</i>
2016	Studied systems formed by PHPA and PEI	Hashmat <i>et al.</i>
2017	Developed PHPA/HQ–HMTA gel systems with resistance to HTHS conditions	Fang <i>et al.</i>
2017	Produced gel systems formed by a terpolymer of AM, AA and AMC16S, crosslinked by PEI	Zhang <i>et al.</i>
2017	Developed systems composed of PHPA, PEI and silica nanoparticles	Ma <i>et al.</i>

(Continued on next page)

Table 2. (Continued)

Year	Activity	Authors
2018	Developed PAM–PEI systems reinforced with nanosilica	Chen <i>et al.</i>
2018	Studied the action of nanosilica as a reinforcement filler in PAM/resorcinol-HMTA systems	Lashari <i>et al.</i>
2018	Developed gel systems with multiple crosslinking, formed by PHPA, Cr(III) acetate and PEI	Jia and Chen
2018	Developed PHPA/PEI systems reinforced with coal fly ash	Adewunmi <i>et al.</i>
2019	Studied the effects of several factors on the gelation performance of hydrogels formed by terpolymer (AM–AMPS–NVP) and PEI	Zhu <i>et al.</i>
2019	Evaluated systems formed by acrylamide-based polymers, PEI, and bentonite	Tessarolli <i>et al.</i>

concentration had a strong influence on the gelation time and the gel strength, since the increase of the terpolymer concentration provided a larger number of sites available for crosslinking, reducing the gelation time and forming stronger hydrogels. The concentration of PEI had an effect similar to the polymer concentration, but less intense. Furthermore, they observed that the molar mass of PEI influenced crosslinking, enabling obtaining hydrogels only in systems produced with PEI with molar masses above 3000 g/mol. The addition of salts slightly shortened the gelation time, and thermally stable gel systems could be obtained at 150 °C.

Tessarolli *et al.* (2019) studied systems formed by acrylamide-based polymers, PEI, and bentonite and evaluated the influence of the polymeric structure on gel strength and gelation kinetics. For this, the following polymers were tested: PAM, HPAM, PAM–AMPS and PAM–AMPS–NVP. The chemical structure of the polymer had a strong influence on the properties. Systems with higher amounts of AMPS or acrylate groups and higher molar masses had greater gel strength and shorter gelation time. Systems with more NVP groups or higher bentonite content had longer gelation time and higher gel strength. Furthermore, the most promising system for application in conformance control was produced with the PAM–AMPS–NVP terpolymer.

The summary of activities performed with acrylamide-based polymers and organic crosslinkers is presented in Table 2. In general, hydrogels formed from organic crosslinkers have advantages over inorganic crosslinking and can be used for conformance control of oil reservoirs with higher temperatures.

3 Conclusion

Conformance control is a key to the EOR method because it stimulates the sweeping of oil in a well-distributed manner in reservoirs. In this technique, the use of gel systems based on polyacrylamide stands out, because they form impermeable hydrogels *in situ* in areas of greater permeability,

obstructing the preferred paths in the rock matrix, and providing greater efficiency in oil recovery. These systems must present good injectivity, low adsorption of their components in the porous medium, controlled gelation time, and stability in the reservoir conditions.

These hydrogels are produced from crosslinking between the polymer and inorganic (metallic ions) or organic crosslinking agents. In systems crosslinked by metallic ions, the formation of the hydrogels occurs by ionic bonds between the negative charges of the polymer carboxylates groups and the multivalent cations, with chromium (III) being used most, generally in the form of chromium acetate (III).

In organically reticulated systems, there are covalent bonds between the amide groups of the polymer and the functional groups of the organic crosslinker. In this case, the use of polyethyleneimine is best because it causes less severe environmental impacts. Due to the greater stability of the crosslinks, these hydrogels have advantages in relation to metal ion crosslinked hydrogels and can be used for conformance control of oil reservoirs with higher temperatures. In general, these systems have gelation time, gel strength, and stability depending on the polymer and crosslinker concentration, molecular weight, degree of polymer hydrolysis, temperature, pH, and salinity.

These gel systems may present limitations for application in reservoirs with severe salinity and temperature conditions. In view of this, nanofillers have been used, generating nanocomposite hydrogels. The results have been promising, with the formation of hydrogels with better mechanical properties and good stability in reservoir conditions.

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