

Polymers for application in high temperature and high salinity reservoirs – critical review of properties and aspects to consider for laboratory screening

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Abstract

A significant amount of oil resides in deep reservoirs characterized by relatively high temperature and high salinity. In such reservoirs, most available chemical fluids for EOR have limited applicability. Even though recent effort has been dedicated to the development of high temperature polymers, there is no clear understanding of what would work best in those harsh environments. In addition, the oil and gas community is also evaluating potential applications of chemical EOR to offshore assets where similar conditions are often found. Field applications in harsh reservoirs have shown limited success in the use of polymers for improved oil recovery. Detail analysis reveals that screening of the fluids was done under ‘model’ laboratory conditions, using non-reservoir core samples and non-representative fluids. These facts have motivated research and development work towards understanding the type of polymers that may be suitable for use in high temperature and high salinity reservoirs and to determine the type of tests to use to assess their performance in a field application for use as lab screening criteria. In this paper, we provide a critical review of the available polymers for application in high temperature and high salinity reservoirs and summarize best practices for their laboratory screening through a recommended workflow.

Keywords: Harsh Reservoirs, Polymer Flooding, Laboratory Screening, Enhanced Oil Recovery (EOR) High Temperature and High Salinity Reservoirs.

Polímeros para aplicación en yacimientos de alta temperatura y alta salinidad – revisión crítica de propiedades y aspectos a considerar para selección en laboratorio

Resumen

Una cantidad significativa de petróleo reside en yacimientos profundos caracterizados por estar asociados a temperaturas y salinidades relativamente altas. Para estos yacimientos la mayoría de los químicos disponibles para EOR tienen una aplicabilidad limitada. Aun cuando recientemente se han reportado esfuerzos en el desarrollo de polímeros para altas temperaturas, aún no se tiene un entendimiento claro de lo que funcionaría mejor en ambientes severos, con alta salinidad. Adicionalmente, la comunidad petrolera está evaluando posibles aplicaciones de tecnologías químicas de EOR en activos costa afuera donde se observan con frecuencia condiciones similares. Las aplicaciones en campo que involucran el uso de polímeros en yacimientos con ambientes hostiles han demostrado un éxito limitado en el mejoramiento de la recuperación de petróleo. Un análisis minucioso revela que la selección de los fluidos se realizó bajo condiciones de laboratorio “modelo”, utilizando muestras de rocas y fluidos diferentes a los encontrados en el yacimiento. Estos hechos han motivado el trabajo de investigación y desarrollo para comprender el tipo de polímeros que pudieran ser adecuados para uso en reservorios de alta temperatura, que presentan fluidos de alta salinidad, y para determinar el tipo de pruebas a utilizar para evaluar su desempeño en una aplicación de campo que podrían utilizarse como criterios de selección de laboratorio. En este trabajo se ofrece una revisión crítica de los polímeros disponibles para aplicación en yacimientos de alta temperatura y alta salinidad, y se reporta un resumen de buenas prácticas para su selección en el laboratorio siguiendo un procedimiento recomendado.

Palabras clave: Yacimientos Hostiles, Inyección de Polímeros, Selección en el Laboratorio, Recuperación Mejorada de Crudo (EOR), Yacimientos de Alta Temperatura y Salinidad.

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Introduction

The increasing global energy demand relies heavily on the use of hydrocarbons; however, the discovery of oil and gas deposits is becoming increasingly difficult with findings in complex and challenging environments. Most of the easily accessed oil is already depleted, and approximately 50% of the initial hydrocarbons remain trapped in the reservoirs. These facts are promoting the evaluation of enhanced oil recovery (EOR) methods as a way to sustain operations and satisfy the energy demand.

EOR technologies refer to a variety of methods aiming to recover stranded oil on partially depleted reservoirs. Some of the methods involve the injection of agents, a fluid or a combination of fluids into the reservoir (e.g.: chemical, gas, thermal and microbial). The injected fluid enhances the oil displacement resulting in lowering of the residual oil saturation. The injected fluids interact with the in-situ rock-fluid system (brine, oil, gas) and may generate conditions favorable for oil recovery, like lowering of the interfacial tension (IFT), inducing wettability alteration, developing preferential phase behavior, etc.

Chemical EOR methods have a long history of field implementation dating back to 1970's. The most popular of these methods is polymer flooding in use in several countries for over 40 years with various degree of success (Needham & Doe, 1987). Most polymer flooding field applications to date were done in reservoirs with in situ-temperature in the range 8°C-110°C, formation permeabilities values between 1 mD and 15 D, brine salinities ranging from 0,1 to 30 % TDS, and oil viscosities in the range of 0,01 cP to 2.000 cP. Polymer flooding is frequently done after waterflooding, attempting to address two types of problems: 1) low volumetric sweep and displacement efficiency, and 2) high residual oil.

The implementation of chemical EOR technologies is always a challenge since they involve multiple processes frequently addressed by several disciplines. In the last three decades, the most significant advances in the development of chemicals for EOR applications are found in the manufacturing of surfactants, polymers, co-solvents and gels. In fact, more new polymers were created in the last 10 years than in the previous 30 years for other oil production applications. Such a development has enabled the industry to consider the use of such chemicals for EOR with incremental recovery in the range of 20-30%; however, the range of application is quite limited based on the reservoir characteristics,

in-situ temperature and brine salinity, and for the high cost involved.

Polymer flooding is one of the most attractive chemical enhanced oil recovery techniques. Its successful application has been related to the existence of favorable reservoir conditions. Most applications have been done in clastics reservoirs, although a few projects were implemented in carbonates. The main reason on the limited application in carbonates is due to challenges preserving the polymer properties at the in-situ high temperatures, and high salinity. Benefits of polymer flooding reported in the literature (Abidin, Puspasari & Nugroho, 2012) refer to the use of Xanthan Gum, PAM (polyacrylamide), HPAM (partially hydrolysed polyacrylamide), and sodium acrylate as co-polymer, for applications where the in-situ reservoir temperature was below 70°C. In general, these polymers enhance the rheological properties of the displacing fluid since the water-soluble polymers can improve the water-oil mobility ratio (Pinto, Herrera & Angarita, 2018), leading to enhanced oil recovery. However, the properties of the polymeric solution render it to be very sensitive to changes such as temperature and salinity, thus when exposed to such harsh conditions as frequently present in some oil reservoirs, new problems and limitations arise when using such standard chemicals (Quadri, Shoaib, AlSumaiti & Alhassan, 2015).

Polymers and co-polymers such as PAM, HPAM and sodium acrylate have been successfully used in certain countries like China, India and Oman. Their popularity is associated to the thickening ability, the flocculation and rheological behaviour in the tested formations (Sheng, 2011). In Daqing, China, water-soluble polymers are in use for over 30 years. The introduction of new polymers, co-polymers and other chemicals made Daqing an excellent place for extensive field trials providing significant learnings on the technology performance to the oil and gas industry, including the ability to use alkali to significantly reduce the amount of surfactants needed in an ASP project and associated cost savings. In the Mangala field, India, ASP floods have been extensively implemented allowing the operator to maintain the target production levels. ASP formulations have been also successfully used in both sandstone and carbonate reservoirs in China and Oman.

More recently, Oil and Gas Majors have started to use polymer flooding in offshore areas like the North Sea, where new polymers specially designed for high-temperature and high salinity environments are being deployed (Hinkley & Brown, 2017)

In this paper, we provide a critical review of the available polymers for application in high temperature and high salinity reservoirs and summarize aspects to consider for their laboratory screening through a recommended workflow.

Available polymers and suitability for use in harsh environments

In polymer flooding, a water-soluble polymer is added to the injected water during a waterflood. The objective is to increase the viscosity of the water phase to improve the efficiency of the displacement. There are three potential ways in which a polymer flood can make the oil recovery process more efficient: a) by decreasing the water/oil mobility ratio; b) through the effect of polymers on the fractional flow, and c) by diversion of the injected water from zones that are already swept. It is well known that when a polymer is injected into a formation containing a stack of heterogeneous layers, crossflow between the layers improves the polymer allocation so that the vertical sweep efficiency is improved (Sorbie, 1991). Another interesting mechanism is related to the polymer viscoelastic behavior. Due to polymer viscoelastic properties, the normal stress between the oil and the polymer solution results in a larger pull force on the oil droplets or oil films. As a result, oil is pushed and pulled out of dead-end pores or disconnected/stagnant pore regions, resulting in a decrease of the oil saturation (Sheng, 2011).

Current available polymers and co-polymers for EOR applications include:

1. Sodium Acrylate (AA): an anionic polyelectrolyte with negatively charged carboxylic groups in the main chain and molecular formula $[-\text{CH}_2-\text{CH}(\text{CO}_2\text{Na})-]_n$. It is primarily used as a thickening agent for its unique ability to absorb and hold onto water molecules, and to combine with other monomers.
 - a. AA cannot withstand high salt concentration, especially in the presence of divalent cations, at high temperatures and under long injection times.
 - b. At temperatures above 70°C, AA moieties hydrolyze increasing the amount of polyacrylic acid in the backbone of the polymer making it very sensitive to hardness. The formation of acrylate groups leads to precipitation and significant viscosity loss (You, et al., 2007) (Levitt, Pope & Jouenne, 2010).
2. Acrylamide (AM): a highly water-soluble vinyl monomer formed from the hydration of acrylonitrile with chemical formula $\text{C}_3\text{H}_5\text{NO}$. Its structure includes one hydrogen bond donor, one hydrogen bond acceptor, and one rotational bond. AM copolymers can be classified into four categories based on their ionic characteristics as non-anion, anion, cation, or zwitterionic compounds (Pei, et al., 2016). The anionicity (degree of hydrolysis) of AM monomers varies from 15% to 40% for commercial AM (Borthakur, Rahman, Sarmah & Subrahmanyam, 1995) (Levitt & Pope, 2008).
 - a. Acrylamide-based polymers and copolymers are unstable at elevated temperatures (>70°C) in hard brine (i.e. water saturated with divalent salts (CaCl_2)) due to hydrolysis of the amide group to carboxylate. The presence of divalent ions promotes the formation of carboxylate complexes that lead to polymer precipitation reducing its useful lifetime (Moradi-Araghi & Doe, 1987). The degree of hydrolysis depends on the acrylamide and hydroxide concentrations.
 - b. For $\text{pH} < 7$, non-dissociated acid groups act as internal catalysts towards acrylamide hydrolysis (Parker Jr. & Lezzi, 1993) and for pH values > 7 two opposite effects can occur according to the pH value: a) an increase in the degree of hydrolysis due to the greater number of hydroxide ions present, and b) a reduction of the hydrolysis rate due to the formation of negatively charged carboxylate residues.
 - c. The degree of acrylamide hydrolysis depends on the temperature and the hydroxide concentration. Ryles reported that temperatures below 82°C are required for acrylamides to remain in brine and avoid precipitation in the presence of divalent cations (Ryles, 1988).
3. Acrylamide Co-Polymers: modified versions of acrylamide co-polymers with other monomers synthesized to improve the limit temperature for precipitation onset in the presence of divalent cations (Parker Jr. & Lezzi, 1993).
 - a. Copolymers of N-vinylpyrrolidone (NVP) and acrylamide have improved stability towards precipitation by divalent cations at elevated

temperatures with respect to polyacrylamides (Doe, Moradi-Araghi, Shaw & Stahl, 1987). Gaillard, et al. (2014) reported that the incorporation of NVP monomers into the polymer chains make it more stable by limiting the degree of hydrolysis, and by bringing robustness at high temperatures (120°C). However, the NVP molecular weight requires more polymer per application (about 3 times the amount of conventional HPAM) making the cost of the process not attractive for operations.

- b. The incorporation of sodium-2-acrylamido-2-methylpropanesulfonate, acrylamido-tertio-butyl sulfonate (ATBS) results in an improvement of the polymer stability up to 120°C (Parker Jr. & Lezzi, 1993) (Sabhapondit, Borthakur & Haque, 2003). These authors explained the enhancement in the hydrolysis when the pH decreased from 8 to 6, due to a decrease in Coulombic repulsion between hydroxide and the polymer. Moradi-Araghi & Doe (1987) found that ATBS does not protect the acrylamide against thermal hydrolysis with consequent precipitation in hard brines. Even though ATBS bring more robustness at lower cost, and lower impact on molecular weight; the stability of ATBS is limited to the temperature range 95°C to 105°C (Moradi-Araghi & Doe, 1987).
4. Polyacrylamide (PAM): a high molecular weight (>106 g/mol) polymer formed from acrylamide and its derivatives. The PAM used in EOR is poly(2-propenamamide) with chemical formula $-\text{CH}_2\text{CH}(\text{CONH}_2)-$. It is a non-ionic, water soluble, and biocompatible polymer that can be synthesized as a simple linear chain or as a cross-linked structure. The cross-linked polymer can absorb and retain large amounts of water because the amide groups form strong hydrogen bonds with water molecules. Even though these polymers are called PAM, they are often copolymers of acrylamide and one or more other monomers. One of the most common comonomers is acrylic acid or sodium acrylate. Poly (acrylamide-co-acrylic acid) and its sodium salt are anionic polymers more effective when used as flocculant and water absorbers (polymerdatabase.com).
 - a. Akbari, Mahmood, Tan, Ghaedi & Ling (2017) evaluated four sulfonate-based polymers (polyacrylamide co-polymers) for stability under high salinity/high hardness conditions.
- The four polymers were basically sulfonated polyacrylamide copolymers of AM (acrylamide) with AMPS (2-Acrylamido-2-Methylpropane Sulfonate). The modified co-polymers showed similar rheological behavior to conventional polymers, except one with a unique behavior, a sulfonated polyacrylamide copolymer AM with AMPS, with a 32 mol % sulfonation degree and high molecular weight found to be less sensitive to salinity and temperature for temperatures up to 95°C, which could possibly make it as a better candidate for enhanced oil recovery (EOR) application in high salinity conditions.
- b. Wu, Mahmoudkhani, Watson, Fenderson & Nair (2012) reported the results of a bench-scale development of new PAM-based polymers with improved performance in harsh conditions. The new polymers were evaluated for their viscosity at various temperatures (up to 120°C) and salinities (up to 180 g/L). After aging at 90°C and 120°C for six months under ultralow oxygen level (< 5 ppb), the viscosity remained relatively stable for the new polymers solutions.
 - c. Rashidi, Blokhus & Skauge (2010) conducted a rheological study of copolymers of AM with PAMS, and HPAM in a NaCl solution and synthetic seawater (rich in divalent ions). PAMS showed better high salt tolerance compared to HPAM. Also, the viscosity and solubility effects of the PAMS were studied as a function of the sulfonating degree and molecular weight. PAM with high sulfonating degree was more salt tolerant, and the effect of divalent ions on viscosity is lower compared to HPAM.
5. Partially Hydrolyzed Polyacrylamide (HPAM): a copolymer of AM and acrylic acid (AA) obtained by partial hydrolysis of PAM or by copolymerization of sodium acrylate with AM (Morgan & McCormick, 1990). HPAM has a coil conformation making it extremely sensitive to ionic environments. Two broad types of HPAM polymers are found in EOR applications: one has a poly acrylamide backbone and the other a sulfonated backbone. HPAM is the most widely used polymer in EOR applications (Manrique, Muci & Gurfinkel, 2007).
 - a. HPAM has been successfully tested at high temperatures (Seright, Campbell & Mozley, 2009). In the absence of dissolved oxygen and divalent cations, HPAM solutions can maintain

- almost half of their viscosity for over 7 years at 100°C, and about 2 years at 120°C. An acrylamide-AMPS copolymer (with 25% AMPS) showed similar stability to that of HPAM over the same period of time. HPAM polymers can be used for temperatures up to 120°C if contact with dissolved oxygen and divalent cations is minimized. In addition, its relatively low cost and good tolerance to mechanical stresses during injection in the reservoir makes HPAM very attractive for EOR applications.
- b. HPAM is very sensitive to the brine salinity and hardness. The viscosity enhancement is significantly reduced when it dissolves in high salinity/hard brine, representing a disadvantage for field application. In the presence of high degree of hydrolysis, the electrolytes present in the brine have a shielding effect on the electrostatic repulsion (Shupe, 1981) (Sukpisan, Kanatharana & Sirivat, 1998).
 - c. High salt concentration and the presence of divalent cations such as Ca^{+2} and Mg^{+2} can cause a reduction in the thickening capability of the polymer due to a contraction of the polymer coils in solution, and in some cases the presence of calcium leads to polymer precipitation (Moradi-Araghi & Doe, 1987) (Ryles, 1988).
6. Salinity Tolerant Polyacrylamide (KYPAM): a copolymer of HPAM that incorporates a small fraction of functional monomers with acrylamide to form comb-like copolymers. These polymers have in their structure an ionic functional group that is tolerant to divalent cations (Luo & Cheng, 1993). In KYPAM, a functional monomer is introduced, and the side chains have both hydrophilic and hydrophobic groups (Sheng, 2011). The flexible chains are stretched, and the KYPAM viscosity is relatively higher than the HPAM viscosity in more saline waters (Luo, et al., 2002). Laboratory measurements indicate that KYPAM is more temperature tolerant, and it has good shear and thermal stability (Luo, et al., 2002).
7. Associative Water-Soluble Polymers (AP). These polymers consist of a hydrophilic long-chain backbone, with a small number of hydrophobic groups localized either randomly along the chain or at the chain ends (Lara-Ceniceros, Rivera-Vallejo & Jimenez-Regalado, 2007). In contact with water, APs are dissolved, and hydrophobic groups aggregate to minimize water exposure. In aqueous solutions at a basic pH, hydrophobic groups form intramolecular and intermolecular associations that give rise to a three-dimensional network that significantly increases the viscosity of the polymer solution at high temperature conditions (Caram, Bautista, Puig & Manero, 2006). The functional groups on this polymer are less sensitive to brine salinity compared to a conventional polymer solution. AP contains both hydrophobic and hydrophilic moieties; therefore, they can resist high salinities and moderate temperatures in comparison to HPAMs.
- a. APs including acrylamide-ATBS and acrylamide-ATBS-hydrophobic monomers have been developed with good performance (high resistance factor) for $T < 95^\circ\text{C}$ at low and high salinities.
 - b. Laboratory evaluation of different APs (Alexis, Varadarajan, Kim, Winslow & Malik, 2016) demonstrated the applicability of these polymers in both unconsolidated and consolidated rocks at different temperatures. Experiments indicate that APs require a lower polymer concentration to generate high resistance factors in porous media and have stable long term injectivity behavior in high permeability rocks (> 1 D). Also, in medium to low permeability rocks (< 300 mD) AP with HPAM backbone have better filterability and injectivity in comparison to polymers with HPAM sulfonated backbone.
 - c. AP can promote intermolecular associations, and thus have enhanced viscosities and resistance factors (Seright, Fan, Wayrik & Wan, 2011). APs showed low-flux resistance factors two to three times the values expected from viscosities. Displacement experiments in long cores suggest that the unexpected high resistance factors could propagate deep into a reservoir supporting enhanced displacement compared to conventional HPAM polymers. APs also show a significantly higher level of shear thinning at low fluxes and a lower degree of shear thickening at high fluxes than HPAM.
8. Rigid Rod Water-Soluble Polymer: polymers with a helical or double stranded conformation which may be considered as a truly rigid rod in solution (Sarkar & Kershner, 1996). These polymers are highly soluble in water and display a shear stable behavior

that can deliver high viscosity at low molecular weight compared to the traditionally used flexible chain polymers such a hydrolyzed polyacrylamide.

- a. Sulfonated water soluble aromatic polyamides, polyureas, and polyimides prepared via interfacial or solution polymerization of sulfonated aromatic diamines with aromatic dianhydrides, diacid chlorides, or phosgene have sufficiently high molecular weight and typically display high intrinsic viscosity and can transform into a helical coil in brine (Sarkar & Kershner, 1996).
9. Zwitterionic Polymers (ZP): polymers characterized by having equal anion and cation groups on the molecular chains, making them highly hydrophilic with antifouling properties. These polymers are called polyampholytes; they are pH responsive polymers (Laschewsky, 2014). The rheology of these polymers can be tuned to the desired rheological properties by changing the pH/ionic strength of the solution, and the temperature dependence of the solution viscosity is minimal. These polymers can enhance the solution viscosity in salt environments up to relevant concentrations (e.g. values higher than 100 g/L TDS). At high shear though, a loss in solution viscosity is observed.
- a. Alcázar-Vara, et al. (2015) showed that ZP had good performance as a multifunctional agent with asphaltene inhibition-dispersion activity as well as an agent to promote the alteration of rock wettability and hence relative permeability, demonstrating that ZP can be used to modify rock wettability to increase the oil recovery in high salinity environments. Martin & Páez (2017) reported the effect of the salinity on wettability alteration and the final recovery performance.
10. Amphiphilic Polymers: are potential candidates for EOR applications due their viscosity resistance in the presence of electrolytes; however, they are impacted by temperature. The rheology of amphiphilic polymers is highly dependent on shear forces.
- a. A novel amphiphilical grafting natural chitosan copolymer (PAMCS) was developed by using one step water-free radical polymerization (Pu, Liu, Peng, Du & Zhao, 2016). The rigid d-glucosamine unit ended having intermolecular association and hydrogen bonding synergistically in the PAMCS solution with good rheological properties, super-high salinity resistance and temperature tolerance in harsh reservoir conditions. PAMCS solution exhibited designed viscosity efficiency and viscoelasticity, and long-term stability in comparison to HPAM.
 - b. Amphiphilic polyelectrolytes or polyampholytes can exhibit a combination of the properties listed in (a). These polymers can have one or two (different) charges and behave as hydrophobes. The rheological properties of these polymeric systems can be tailored by careful molecular design, i.e. by selecting the ratio of the different monomers in the structure. According to the molecular design the polymers could be pH-responsive, temperature insensitive or salt resistant. For certain conditions, i.e. low pH and high electrolyte concentration, carboxylic groups lead to better responsive polymers when compared to polymers having sulphonic groups.
 - c. An amphiphilic copolymer based on Polyethylene glycol-methyl-ether acrylate (PEGA) was developed by Atomic Transfer Radical Polymerization (Raffa, Broekhuis & Picchioni, 2016). The measured viscosity and surface activity of polymers solutions in pure and salty water indicate that the new polymer is an effective surface active viscosity agent, so it could be a good candidate as polymeric surfactant for EOR applications
11. Xanthan Gum: a biopolymer (polysaccharide) produced by the fermentation of glucose or fructose (Leela & Sharma, 2000). The Xanthan molecule displays two glucose units, two mannose units and one glucuronic acid unit (Garcia-Ochoa, Santos, Casas & Gomez, 2000). The side chains of the Xanthan polymer have charged moieties (pyruvate groups) allowing the polymer to behave like a polyelectrolyte polymer; however, its thickening behavior does not have a strong dependence with salinity; it is a consequence of the high molecular weight which range from 2 to 50,000,000 g/mol.
- a. Xanthan gum can resist temperatures up to 80°C and relatively high shear forces up to 5000 s⁻¹. Xanthan starts to lose its thickening properties above 100°C (Kierulf & Sutherland, 1988) (Chen & Sheppard, 1980) (Seright & Henrici, 1990).
 - b. Xanthan is susceptible to bacterial degradation. Salt tolerant aerobic and anaerobic bacteria

can degrade Xanthan resulting in a loss of its thickening ability (Hou, Barnabe & Greaney, 1986). Biocides are used with this polymer to mitigate degradation.

- c. Scleroglucan: a non-ionic triple helix polysaccharide produced from the fermentation of a pathogen fungus. The backbone consists of linearly linked β -1,3-D-glucose chains. It is a class of polymer with good performance under harsh conditions, with no change in viscosity or injectivity at 95°C and only 25% drop in viscosity after exposure to 115°C for up to six months. Scleroglucan is stable in the presence of hydrogen sulfide and ferrous species (Jensen, et al., 2018). A pilot test is being conducted to evaluate the long-term stability of the polymer, and to assess the injectivity control and incremental recovery (Jensen, et al., 2018).

12. Other Polymers:

- a. A new class of synthetic polymers NVP-free, having different content of ATBS and high thermal stability up to 140°C was designed for use in harsh conditions such as those found in reservoirs in the Middle East characterized by high salinity brines (total dissolved solids, TDS > 220 g/L) was reported by Dupuis, Antignard, Giovannetti & Gaillard (2017). These polymers were tested in coreflooding experiments showing good performance. They were more stable than ATBS or NVP polymers and could be used in sandstones and carbonates (permeability in the range 100-700 mD).
- b. Quadri, et al. (2015) reported a polymer screening study for carbonates under harsh conditions. They evaluated HPAM, copolymers of acrylamide and ATBS, terpolymer of acrylamide, ATBS and NVP, and one non-ionic, water soluble homoglucon polysaccharide (biopolymer described by Quadri, et al. (2015). Polyacrylamide based co- and ter-polymers showed good thermal stability under low salinity conditions. A biopolymer (polysaccharide) displayed good thermal stability (up to 120°C) and high salinity tolerance (up to 220 g/L) under anaerobic conditions for over eight months with non-significant loss in viscosity. In addition, the adsorption of the biopolymer decreased with increasing salinity and temperature.

- c. Dai, et al. (2017) developed a novel thermal-resistant and shear-stable amphoteric polyacrylamide (PASD), using AM, sodium styrene sulfonate (SSS), and acryloxyethyl trimethylammonium chloride (DAC) monomers, prepared by free-radical polymerization in high-salinity solution. This amphoteric polyacrylamide exhibited excellent salinity and high temperature tolerance. The reached viscosity retention was near 40% at 120°C.

- d. A synthetic hydrophobically modified hydroxyethyl cellulose (HEC) was developed using Bromo-dodecane (BD-HMHEC) (Liu, Mu, Wang & Wang, 2017). The rheological properties and oil displacement efficiency was tested for Daqing reservoirs. Results showed that BD-HMHEC solution had good thermal-resistance (90°C) and salt-tolerance (up to 100 g/L), improving the oil recovery by 7–14% in comparison with HEC flooding at concentrations of 4 g/L under equivalent conditions.

- e. A class of the water-soluble ZP temperature-responsive exhibits a volume phase transition at a given temperature, causing a sudden change in the solvation state with low critical solution temperature (LCST) and resistance to high temperatures (90°C); however, these fluids are susceptible to phase separation which may lead to a significant drop in the viscosity. The solubility of these polymers decreases with temperature below the LCST (Fan, Boulif & Picchioni, 2018).

The properties of a good polymer have been summarized by several authors and include Sheng (2011):

- a. No –O– in the backbone (carbon chain) for thermal stability
- b. Negative ionic hydrophilic group to reduce adsorption on rock surfaces
- c. Good viscosity ability
- d. Nonionic hydrophilic group for chemical stability

As presented, it is clear that most available polymers can be used in reservoirs with relative mild temperature and salinity conditions. For other reservoirs exposed to more severe conditions (temperature > 95°C, salinity > 90 g/L) standard polymers like AM, PAM, and HPAM cannot be used, and the promising newly developed polymers include modifications to AP, thermal associate

polymers and HPAM functionalized with AMPS monomers.

Polymer laboratory screening

EOR candidate polymers must provide the required rheology at minimal concentration, be thermal,

mechanical and chemically stable, and have low adsorption to the rock. In this section, we summarize some of the key aspects to consider when doing a laboratory polymer screening. In general, the series of steps followed for laboratory polymer screening can be summarized in a schematic workflow as shown in Figure 1.

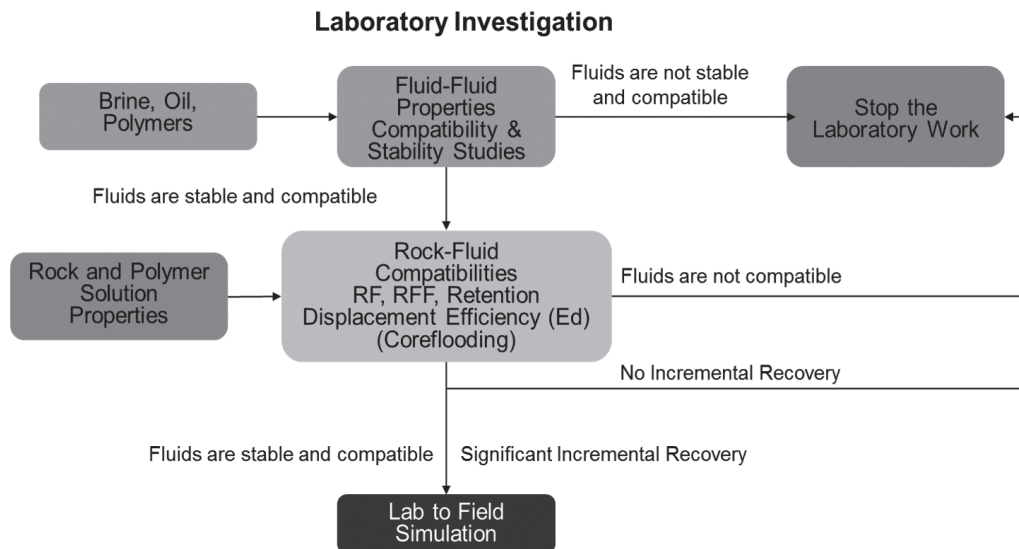


Figure 1. Workflow for polymer laboratory screening.

It is assumed that a preliminary EOR screening exercise has been completed at a project level taking into account the reservoir properties, field location and logistics, and a calculation of the floodable pore volume with a high-level economic estimation for the lab screening is available. It is a good practice to consider the basic reservoir engineering screening criteria for polymer field application which includes: a) making sure that the candidate reservoir has a reasonable good waterflood performance, b) actual average permeability > 25 mD with no extreme variations, c) sufficient remaining oil saturation (and a good understanding of its distribution), d) water chemistry is known, e) crude oil viscosity < 5,000 cP, f) understanding of the impact of any nearby aquifers, and g) good understanding of available facilities (sufficient injection capacity).

Figure 2 shows a recommended laboratory workflow generated based on best practices from the literature and our own experience. To evaluate polymers performance, the recommended approach includes: rock and fluid selection and characterization and the execution of displacement experiments at expected reservoir conditions, here represented by high temperature and salinity.

Step 1: Assessment of the Required Conditions for Lab Screening and Polymer Pre-Screening.

In general, the screening process starts with the selection of commercial available polymers (most laboratories usually test between 5-6 different types of polymers) according to their temperature stability, salinity tolerance, quality of mixing brine, and costs. A series of tests are done to understand the polymer properties at reservoir conditions including evaluation of the fluid rheology based on the response of the viscosity vs. shear thinning (Veerabhadrapa, Urbissinova, Trivedi & Kuru, 2011), evaluation of the molecular weight vs. molecular weight distribution (poly-dispersivity), determination of polymer anionicity, and filtration ratio tests to select the most viable candidates for the formal screening process that includes the polymer performance evaluation through core flood experiments. The results from these tests are analyzed and a candidate ranking is proposed for subsequent evaluation. These tests are done using standard laboratory protocols not discussed in this article.

The conditions at which the injected fluids will be exposed are critical for the success of the process. A

good understanding of the reservoir including depth, in-situ pressure, temperature, formation properties like porosity, permeability, pore size distribution, wettability, in-situ fluids play an important role in the process performance. Facilities inputs are also very relevant

such as potential injection capacity. If the application is intended to follow a waterflood, it is important to analyze the composition of the produced water for use in the testing.

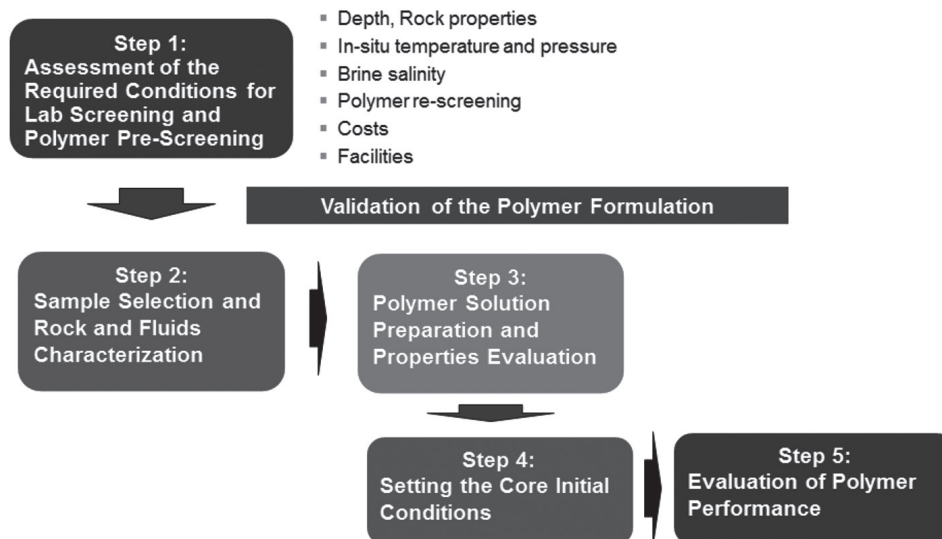


Figure 2. Proposed workflow for polymer screening and evaluation.

Step 2. Sample Selection and Rock and Fluids Characterization

Reservoir representative fluids should be used in the tests wherever possible. Live oil is generally preferred; however, if not available, dead oil should be restored at reservoir conditions. Crude properties like viscosity, density, composition at in-situ conditions, total acid number (TAN), SARA and sand and water content (BSW) are in general very useful in the interpretation of the experimental tests. Use of filtered oil is recommended to minimize potential plugging. For the brine attention is needed to make sure it describes the chemistry and properties of the produced water (density, total dissolved solids (TDS), turbidity, pH, and conductivity). McPhee, Collin & Zubizarreta (2015) recommend that the brine be stored if it is not used immediately.

Rock samples should be representative of the reservoir where the polymers will be applied and be cleaned of residual solids and fluids normally done through flushing, flowing, or by contacting with various solvents to extract hydrocarbons and/or brine (API RP40, 1998). Information about properties like porosity, permeability, mineralogy, and wettability allows to understand the physics of the flow and transport phenomena during the polymer injection. Recommended practices on how to

do wettability restoration is available in the literature (Araujo, Araujo & Molinaris, 2018).

Step 3: Polymer Solution Preparation and Properties Evaluation.

For the laboratory tests the polymer solution should always be homogeneous. According to the nature of the polymer product for use (fermentation broth, gel or powder) a slightly different mixing method is used to prepare the solution.

Polymer hydration. The preparation of a polymer stock solution, regardless of polymer type, should follow the API RP 63 (1990). According to this standard, the first step is to prepare a stock solution with 5,000 ppm of polymer concentration followed by dilution to obtain the desired polymer concentration. Some recommendations regarding the mixing process to avoid agglomeration of particles are available in the literature (Rashidi, et al., 2010) (Yerramilli, Zitha & Yerramilli, 2013) (Akbari, Mahmood, Tan, Ghaedi & Ling, 2017). The polymer should be hydrated in a glove box to prevent contact with oxygen. Once prepared the polymer solution should be filtered under pressure (usually 15 psi) through cellulose filters (conventional polymers) or polycarbonate filters (APs) and properly stored till its use.

Appropriate storage: Polymers stored at room temperature tend to degrade over time as they deteriorate due to many reasons including bacteriological action (Escudier, Clement-Evans & Poole, 2005), it is a good practice to use a fresh polymer solution for the experiments. The lifetime of storage polymer solution is quite variable. Anionic and nonionic polymers last longer once dissolved but the presence of certain contaminants like ferrous iron can reduce the solution life significantly. Cationic polymers have the shortest storage lives since they can hydrolyze once dissolved. Attention should be given to hydrolysis since it reduces cationicity. If the polymer samples are dissolved in advanced of their use, mitigations should be in place to minimize any chemical or physical changes that might result from their storage (Escudier, Clement-Evans & Poole, 2005).

Polymer characterization. Even though polymer properties like molecular weight, anionicity, solubility, etc., are provided by the manufacturer, it is always recommended to validate the data through laboratory measurements since commercial product properties may change over time.

Polymer molecular weight (Mw) plays an important role in the evaluation of the polymer's performance in EOR applications since the polymer properties are influenced by the molecular weight distribution. A variety of methods are available to measure Mw including gel permeation chromatography (Holzwarth, Soni & Schulz, 1986), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (Yalcin, Dai & Li, 1998), and Nuclear Magnetic Resonance (NMR, Izunobi & Higginbotham, 2011).

Polymer anionicity, also known as hydrolysis degree, can be evaluated by ^{13}C NMR spectroscopy and C, N elemental analysis (Zurimendi, Guerrero & Leon, 1984) or colloid titration based on the stoichiometric combination of positive and negative colloids where the endpoint is decided by indicators (Terayama, 1952).

Polymer concentration and residual monomer content can be measured using several methods including: a) SEC-MALS with Mw measurement and NMR, b) UV-VIS spectroscopy – a fast and simple method (Gibbons & Örmeci, 2013), c) the start tri-iodine method for water soluble polymers containing primary amide groups (like HPAM) and associative polymers (Scoggins & Miller, 1979), or d) the turbidimetric method that uses a reagent that react with some polymer components (like AMD subunits in PAM/HPAM) to produce insoluble

colloids that remain suspended in solution, giving rise to turbidity (Kang, et al., 2014).

For viscosity measurements, a high precision instrument is recommended, like a low shear rheometer equipped with either an ultra-low adapter or small sample adapter. It is important to evaluate the viscosity as a function of polymer concentration and temperature at the optimal shear rate. The protocol associated to the viscosity measurement depends on the type of instrument used; for most common rheometers procedures are described in the API RP 63 standard (1990).

The rheological characterization should be done on selected polymer solutions for a specific concentration and filter ratio tests. In general, viscosity is measured at shear rates ranging from 0.1 to 500 s^{-1} for concentrations (ppm) ranging from 0 to 5,000. It is also important to evaluate the effect of brine hardness and pH on the viscosity. For the brine hardness, the idea is to quantify the effect of increasing salinity on the viscosity according to the degree of hydrolysis.

Polymer solubility can be assessed by: a) low cost visual determination based on visual detection of when the fluid enters a two phase region, captured as noticeable cloudiness (Wolf, 1985); b) viscosity measurements based on the difference in viscosity between different solutions; c) differential scanning calorimetry – a method that requires high level of expertise for data interpretation; d) gas liquid chromatography has also been used DiPaola-Baranyi & Guillet (1978) due its capability of characterize the polymer-solvent system and to investigate the interaction between polymers and non-solvents; and e) the fluorescence probe approach based on an aggregation-induced emission (AIE) is considered as an accurate method for measuring the solubility parameters of a polymer (Jian, Huang, Wang, Tanh & Yu, 2016).

Filterability is an important test to ensure that a polymer solution is free of aggregates which could lead to formation plugging. The standard procedure to run the tests is described in the API RP 63 Standard (1990) using a high-pressure filter press. Levitt (2009) presented an overview of the filtration procedures, filter size and material adequate according to the polymer type. It is important to consider that filtration ratio tests are in general not conclusive as screening tests when using associative polymers. Previous findings (Alexis, et al., 2016) indicate that AP can show low filter ratio; however, lower polymer concentration is required to generate high resistance factors when used in porous media. For biopolymers, a modified API RP 63 method

is used for testing at low pressure to get an acceptable filtration time (Jensen, et al., 2018). In this method the pressure is hold between 1.5 to 3 psi to get 2 to 4 minutes of filtration time with solutions at 50 cP at 10 s⁻¹.

Another important aspect to consider is the environment where the short/long term thermal stability tests are done, which is recommended to be oxygen free (< 10 ppb) conditions. Tests are conducted at the selected optimal viscosity and polymer solution concentration. The degree of compatibility between the polymer and the brine is assessed by the change in the appearance of the polymer solution as well as the change in viscosity during the aging test. A clear single-phase aqueous solution at both ambient and reservoir temperature are expected for the good polymer candidates, and the polymer viscosity should not decrease significantly during the test duration. Since temperature in general has a significant impact on the polymer behavior, thus the tests should be done at reservoir temperature if possible. Two setups can be used to minimize testing errors: 1) the polymer samples are dispensed into air-tight vials (ampoules) inside of an oxygen-free environment created using a glove box, and periodic visual inspections and viscosity measurements are recorded at selected time intervals, and 2) the solution is transferred into small Hastelloy cylinders with a large enough volume for the viscosity measurements at the specific time points of the thermal stability analysis while all measurements are done in an oxygen-free atmosphere.

Shear stability can be evaluated in two different ways: i) using the API RP 63 (1990) and ii) shearing the polymer solutions at high rpm (usually 30,000) for different time intervals at constant temperature. Viscosity monitoring at each interval allows assessing shear degradation.

Step 4: Setting the Core Initial Conditions

If the field where the polymer flooding is to be applied follows a waterflood, the core sample should be submitted to a similar saturation history by injecting a similar amount of water (in terms of porous volume (PV)) as done in the field starting from reservoir native saturation conditions.

Step 5: Evaluation of Polymer Performance

Polymer performance is evaluated through coreflooding experiments at reservoir conditions. The experimental set-up typically consists in an injection system, transfer cylinders, core holder, backpressure regulator and effluent collector. High precision differential pressure

transducers should be used to measure the pressure gradient across the cell. A backpressure regulator (BPR) is frequently placed on the downstream side of the core to help dissolve any air that may remain within porous medium before flooding. It is a good practice to remove the BPR prior the polymer injection to avoid polymer degradation. In addition, the use of pressure taps along the core can provide representative data to assess the polymer behaviour.

Important variables to design the polymer flooding at lab scale are: flow rate, temperature, confining pressure, back pressure, initial water saturation, rock permeability, and effluent properties. Very accurate instruments/sensors are required to assess the values of these parameters. Parameters determined through coreflooding include: permeability, initial water and oil saturations, PV and inaccessible PV, injectivity, RF (resistance factor) and RRF (residual resistance factor), adsorption/retention, slug size, and effluent characteristics.

Injectivity is measured using the pressure drop when the polymer is injected into the rock. The selected polymer must have a good injectivity (minimum pressure-drop) to allow rapid displacement and recovery of oil. The pressure drop is also used to estimate the permeability reduction, and viscosity measurements during flow allows the calculation of RF and RRF. Resistance factors versus polymer solution throughput should be used to analyze the potential of plugging.

Polymer retention is another quantity to pay attention since it delays polymer propagation through the porous formation. High polymer retention can substantially delay oil displacement and thus limit the oil recovery during a polymer flooding. Two types of adsorption/retention mechanisms need to be considered: i) mechanical retention associated with the relative size of the polymer molecule and the pore dimensions, an irreversible process, and ii) physicochemical adsorption, which is reversible and associated to the chemical and physico-chemical characteristics of the polymer and the rock. Many methods have been reported in the literature to measure polymer retention and inaccessible pore volume (Seright, Seheult & Talashek, 2008) (Domenico & Schwartz, 1990) (API RP63, 1990) (Chiappa, et al., 1999).

Experimental results are used in numerical simulation to design polymers slugs for field application. Molano, Navarro & Díaz (2014) developed a methodology to design polymer slugs for polymer injection process based on rock- fluid interactions phenomena in porous media,

focusses on the behavior of the polymer concentration on the injected fluid as a function of time and length; and how interaction phenomena within reservoir affects its performance.

When evaluating polymer flooding performance for harsh reservoirs, the effluent must be analyzed using the appropriate tools. At least the following tests should be completed: TDS, salinity, dissolved oxygen, pH, conductivity, hardness, polymer concentration, and viscosity. Effluent analysis is used to evaluate the polymer retention, inaccessible pore volume and rheological properties. In addition, the effluent parameters can help to identify issues or problems early on the study before extensive lab work is undertaken.

The described workflow works well with most of the standard polymers presented in the previous section. However, when evaluating polymers for use in hostile environments of high temperature and high salinity, further attention is required in particular to the type of instrumentation used in the laboratory. Some aspects to consider include:

- a. coreflooding system – the wetted parts (coreholder, fluid cylinders, and lines) made from a corrosion resistance material like Hastelloy. The high salt content and the presence of iron in the system could cause corrosion;
- b. the coreflood system (coreholder, flow lines, capillary viscometer, fluid accumulators, etc.) placed in a constant temperature environment like the one provided by a convection oven.
- c. Coreflooding parts like core sleeves and O-rings need to be compatible with the environment. The widely used Viton sleeves and seals made from a fluorocarbon elastomer perform well in the presence of organic fluids like hydrocarbons and other solvents over the temperature range from -7°C to 205°F. For harsh environments the use of AFLAS (a copolymer of tetrafluoroethylene and propylene) material is preferred;
- d. Injected fluids should be exposed to minimal temperature variations; therefore, fluid accumulators should be placed inside an over and preferably closer to the coreholder.
- e. Viscosity measurements are recommended to be done with a capillary viscometer for the rheological evaluation during the polymer flooding
- f. For effluent collection, it is recommended to use accurate fraction collectors and high precision instruments for evaluation of dissolved oxygen (precision of at least 1 ppb), and accurate titrators for the polymer concentration. We recommend using ion chromatography (IC) instead of an electrode probe to evaluate the salinity when working with polymers exposed to a harsh environment.

Discussion and conclusions

Identifying a polymer that can withstand high-temperature and high-salinity conditions is a major step for a successful polymer-flooding application (Hashmet, AlSumaiti, Qaiser & AlAmeri, 2017).

From the polymers available for EOR, sodium acrylate and polyacrylamide based co-and ter-polymers are found to be stable only under low salinity conditions and in most cases they can resist temperatures up to 70°C. Modified acrylamide co-polymers have improved stability under harsh conditions, however the amount of polymer required to obtain a good recovery is generally too high, around 3 times the amount required for conventional polymers, so their use may be not attractive for commercial applications. Sulfonate base acrylamide co-polymer (ATBS) is an option for temperatures below 105°C. PAMs have showed better high salinity and temperature tolerance than HPAMs which showed relatively good stability only when the dissolved oxygen is extremely low and if divalent cations are minimized. A salinity tolerant polyacrylamide has been developed (KYPAM) but requires additional field testing. Associative polymers seem to be an option for high salinity environments, however further improvement is needed to increase the temperature application limit.

Other polymers like zwitterionic polymers are resistant to high TDS (~ 100 g/L) and can be used as a wettability modifier to increase the recovery factor. Biopolymers like Xanthan gum can resist temperatures up to 100°C with limited tolerance to high salt content could be impacted by bacterial degradation. Scleroglucan has high salinity tolerance up to 200 g/L. These types of polymers are potential candidates for applications in certain types of reservoirs but they all need to be field tested.

A more promising candidate for harsh reservoir is a synthetic polymer NVP-free with ATBS content due its thermal stability up to 140°C and salinity tolerance (up to 220 g/L) tested for carbonates with a good performance. We expect future work to continue on the improvement of the polymer properties.

The laboratory screening process typically starts after a pre-screening phase that provides the required data to understand the behavior of the polymers at the tested conditions. It is important to consider the polymer chemical structure since the rheological properties are affected by the chemical structure and the external parameters.

When screening for the polymers under harsh conditions important points to pay attention are: a) impact of salt - the viscosity of the polymer should decrease as the salt concentration increase, b) analyze the polymer rheology since a thermal degradation may occur at high temperature, c) since different polymers display different behavior when they are mixed with brine it is recommended to use the hydration method suggested by the vendor, and d) high salt contents result in a strong molecular interaction in the polymer solution, and when the salinity is very high the solubility of the polymer might be compromised, forming a different structure.

Regarding the polymer performance careful evaluation of the results is required before proceeding to the polymer ranking and selection. Some experimental results could be difficult to interpret. For example, higher values of RF and RRF factors could be attributed to gel-type effects in aqueous solution, resulting in an increase in mobility retardation. Also, when Fe^{+2} is present with dissolved oxygen, the viscosity of the polymers can decrease due free radicals attack (Fenton reaction) even at low temperatures (25°C) making difficult to understand the viscosity behavior (Pope, et al., 2014). For this reason, we recommend using all available results from the polymer ranking exercise rather than discarding a particular polymer based on the result from one single test. Just as an example, associative polymers are sometimes rejected based on the outcome from the filtration ratio test; however, these polymers show reasonable good performance in core flood experiments, which are more representative of what may occur in the field application.

We emphasize that for carbonates in harsh reservoirs the restoration is particularly important since the carbonate rock can become more oil-wet when exposed to increased concentration of divalent cations in the brine. Thus, aging in reservoir oil aims to preserve injectivity and reduce the retention on the rock surface (Dupuis, et al., 2017).

Finally our message can be summarized as: To be successful in a polymer injection project it is important to set clear objectives, gather the required

reservoir information, have the resources to conduct all the required tests, perform careful QA/QC of the results, use best practices to obtain high quality data, to document properly, and to use all the available information and results to understand the polymer behaviour before making a final decision on the ranking of the polymers.

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