

## Pushing the Envelope of Polymer Injectivity in Low Permeability Sandstones

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### Summary

Chemical EOR is one of the more attractive methods to improve oil recovery. Numerous successful projects including injectivity tests, pilots and full-field developments have been executed without major injectivity issues or decline. Nevertheless, this topic remains a concern among operators.

Polymer Flooding has seen more interest from the industry, and more challenging reservoirs (low permeability formations) are considered—thus raising concerns about injectivity. Filter ratio is routinely used as an injectivity screening criteria, but does it correlate with polymer injectivity and propagation during coreflood experiments, especially in the presence of crude oil? This paper provides new insights on polymer injectivity in cores considering polymer molecular weight, chemistry, rock permeability and mineralogy. The results are obtained from dedicated experiments and examination of several extensive data bases (including the literature).

State of the art commercial polymers of varying chemistry with molecular weight ranging from 5 to 27+ MDa were injected into different sandstone cores having permeabilities between 10 to 200 mD with a range of clay content. Filter ratio was also determined and compared to injectivity in cores. All the data comes from field project case studies using reservoir cores and representative outcrop cores.

For HPAM, injectivity was not a concern. It was possible to propagate up to 27+ MDa HPAM in a 100-200 mD core without significant pressure build-up. Concerning ATBS polymers, injectivity initially appeared to be constrained by the ATBS content; a 15 MDa polymer with a medium-high ATBS content poorly propagated below 200 mD. However, optimization based on molecular weight for similar ATBS content showed stable propagation in representative porous media. Finally, the filter ratio test did not always correlate to injectivity. Indeed, it was observed that several 1.2  $\mu\text{m}$  FR tests (performed on high Mw polymers) failed despite successful transport in cores having permeability below 200 mD.

In addition, acrylamide-based terpolymers allowed improvement in transport of ATBS polymers - a 20 MDa polymer containing medium level of ATBS was able to propagate in less than 100-mD cores. These observations are applicable to cores having clay content below 5%. For higher clay content, injectivity should be assessed case by case using reservoir core and crude oil.

This paper establishes new references in terms of polymer transport behavior in porous media and highlights the importance of appropriate selection of polymer, polymer quality and experimental protocols to properly assess polymer injectivity in cores.

Significance of the proposed paper:

1. Extensively examines the lower limits of permeability for injection of synthetic polymers, especially as a function of polymer molecular weight, polymer composition, rock mineralogy, and the presence of residual oil.
2. Better characterizes the relations between filter ratio, permeability and polymer injectivity in low-permeability rock.

## Introduction

Polymer flooding is a well-established enhanced oil recovery (EOR) technique that is typically applied after or in place of a waterflood. From an oil recovery perspective, water injection helps in re-pressuring the reservoir and recovering oil; however, inherent permeability contrast and high mobility difference between oil and water can result in channeling and reduced recovery efficiency. Polymer flooding is the EOR process whereby water-soluble polymers, typically derivative chemistries of polyacrylamide, are used to increase the viscosity of injection brine, thus reducing the mobility of the injected fluid relative to the oil and hence improving the recovery process.

Implementation of polymer flooding projects to recover oil from all rock types has garnered more attention in the last two decades. More recently, the boundaries are being pushed by pursuing low permeability, oil-bearing formations that represent large resources and only have been produced under primary and/or early waterfloods. Historically, low permeability reservoirs were considered to be candidates for future recovery technologies, since they were deemed too low permeability for polymer flooding. Recently, polymer flooding in these types of reservoirs are being reconsidered and the value proposition is appealing. As operators look to improve energy efficiencies, synergies and reduce environmental impacts, the ability to inject polymer into tighter rock formations will become an increasingly attractive way to sustain oil production beyond waterflood operations.

One of the key questions for implementing polymer flooding in lower permeability reservoirs is related to the field injectivity or throughput capability if offset production is optimized. The ability to inject polymer is commonly compared to waterflood injectivity, regardless of whether offset breakthrough has occurred or not. Key variables to be considered that may impact polymer injectivity, namely – debris in the solution, polymer solution rheology and mechanical degradation of the polymer (Seright et al., 2009). An injectivity analysis suggested that even if near wellbore oil saturation was very low and permeability to water was high, the viscous nature of polymer will substantially reduce injectivity (to one-fifth or less of the injectivity of the waterflood) if fractures or fracture-like features are not open at the well. Additional review papers by Glasbergen et al. (2015) and Delamaide et al. (2014) on application of EOR technologies in low permeability reservoirs affirmed similar caveats impacting injectivity. Thomas et al. (2019) reviewed a number of field injectivity projects and discussed field cases where injectivity was similar to that of waterflood, or better-than-expected injectivity was achieved by carefully controlling injection rate and limited fracture propagation. However, an important goal is to determine the permeability limit that polymer can be effectively injected into and propagate through, to achieve improved, long-term polymer EOR production.

### Laboratory Studies on Polymer Transport in Low Permeability Porous Media

Early studies discussed the adoption of polymer to viscosify injection water. Sandiford (1964) demonstrated through a series of linear and radial laboratory corefloods that low concentrations of partially hydrolyzed polyacrylamide polymers (HPAMs) could be used to displace a range of oils with viscosities ranging from 2 to 325 cP. Resistance encountered during injection of large polymer macromolecules into rocks is due to the frictional energy of the polymer molecules, but also due to their flexibility and ability to deform and stretch. If the time taken by the polymer to relax from a stretched state is longer than the transit time to the next pore constriction, higher is the elastic behavior; hence, the elongational viscosity can dramatically increase especially when traveling through different sized tubes and pore spaces (Marshall and Metzner, 1967). Upon consideration of this type of flow behavior, Hirasaki and Pope (1974) were able to successfully model polymer flow behavior by utilizing a dimensionless pore reduction parameter representing the ratio of polymer coil size relative to effective pore radii. The authors allude to the importance of being able to correlate changes in intrinsic viscosity, adsorption, permeability reduction as a function of polymer type, brine composition and rock properties.

Another study (Seright, 1983) showed that beyond a critical velocity in porous media, polymer molecules undergo mechanical degradation and yield an increased entrance pressure effect; however,

in a separate paper it was demonstrated that mechanical degradation primarily affects larger molecular weight species (Seright et al., 1981). Although filtration or shear degradation that may eliminate the low-shear rate viscoelasticity effects in high permeability media, field shear history of the polymer may be a more important consideration when trying to optimize polymer chemistry type, molecular weight, and viscosity for a reservoir of lower permeability.

In a series of papers, Zitha et al. (1995, 1998, 2001) discussed the flow behavior of PAM (10-11 million Daltons, nonionic) and HPAM (8-10 million Daltons, 27% hydrolysis) in both low (140-mD, 3- $\mu$ m pore diameter) and high permeability (3,200-mD, 16- $\mu$ m pore diameter) using sandpacks of silicon carbide (SiC) powder. In the low permeability packs, the mobility reduction or resistance factor of the 340-ppm PAM solution was found primarily from the pore-size reduction due to polymer adsorption of a single polymer layer. Therefore, bridging occurred mainly in smaller pores than larger pores and at lower critical velocities. The authors identified three key conditions where continuous build in resistance factor would be observed – i) permeability and pore-throats are sufficiently small, ii) the velocity gradient in the rock exceeds the elongational flow threshold and iii) where adsorption mechanisms are sufficiently present – however, if one of these conditions is eliminated, steady-state flow could be achieved.

During a series of flow tests using freshly made HPAMs, Seright et al. (2010b) observed evidence of increasing resistance factors at low flux to occur only in low permeability 55-mD Berea outcrop sandstones. However, when polymer was injected through a similar permeability core at a fixed rate of 1.6 ft/d, collected and reinjected into a second Berea core of similar permeability, the high resistance factor effects and shear thickening at low rates were not observed. Follow-up flow experiments introduced the ratio of minimum resistance factor, relative to the low-shear, Newtonian viscosity, with unity indicating no increase in resistance factor effects compared to shear viscosity. A unit ratio was observed for all MW polymers injected in porous media of permeability 269 mD and higher; however, in the 55-mD Berea, as the molecular weight injected was increased, a maximum ratio of 6.3 was calculated for a 20-22 million Dalton HPAM. Subsequent injection of a 6-8 million Dalton HPAM reversed the ratio back down to 1.3, suggesting reversible hydrodynamic retention effects. The authors commented that the reversible nature of the resistance may potentially diminish as permeability decreases below 20 mD.

### **Field Cases of Polymer Injection in Low Permeability Reservoirs**

The injection of polymer into low permeability, oil bearing reservoirs have been trialed in several instances in the documented literature. An early review paper by Jewett and Schurz (1970) discussed several pilot and commercial polymer flood applications that were conducted between 1964 and 1969. The projects were further identified by polymer injection performed after primary, early or late secondary, or following waterflood economic limit - in tertiary mode. Interestingly, successful polymer flood projects were found to exist over average permeabilities ranging from 20 to 2,300 mD; however, it was noted that a rule-of-thumb, low-end cut-off was below 50 mD. This limit was primarily attributed to an injectivity constraint. If transport is acceptable, and throughput can be maintained through injectivity, the process is sustainable and could be applied in lower permeability formations. This included early trials reviewed by Pye (1964) where a polymer field pilot in the Niagara field injecting a 1.35-cP polymer for 33 months into a Pennsylvanian sandstone averaging 20 mD and containing 16-cP light oil. Comparative analyses of the waterflood patterns in the area were performed and the volume of oil recovered at the economic limit was found to be nearly double for polymer flood vs. waterflood. Castagno et al. (1987) reviewed the lab-to-field evaluation of a polymer flood project in the Tensleep reservoir of the Big Horn Basin in Wyoming, USA. The authors estimated a 5 million STB (2% OOIP) increase due to mobility control alone if a unit viscosity ratio polymer solution could be injected in a reservoir with permeability ranging from 6 mD to 137 mD. Haynes et al. (2013) describes a project where a HPAM polymer was injected into an average 5-mD, high clay content, and legacy waterflooded Windalia reservoir in Australia. A 16 million Dalton, 12% hydrolysis HPAM injected at concentrations ranging from ~400 ppm to 1,000 ppm without any injectivity issues resulted in-depth flow diversion from fractures to deeper parts of the reservoir.

This study aims at better understanding the limits of injectivity of partially hydrolyzed polyacrylamides (HPAM), ter-polymers containing sulfonated acrylamide (HSPAM) and partially sulfonated polyacrylamides (SPAM) conducted in sandstones in the permeability range between 10 and 200 mD. The scope of the study will particularly emphasize the influence of the ATBS content and the molecular weight of the polymer on its injectivity behavior, while keeping salinity and temperature constant. Mineralogy variation was also studied over the permeability range tested. The systematic evaluation of polymer flow behavior in these low-permeability, sandstone outcrops have helped to identify polymer transport limits; thus, potentially pushing polymer flooding viability to lower permeability reservoirs.

## Materials & Methodology

Most of the data reported in this paper were selected from ongoing field evaluation projects and based on rock mineralogy, temperature and brine salinity. Data acquired at two different temperatures and brine salinities were included as part of the injectivity studies in cleaned, representative outcrop rocks. The experimental protocols for polymer solution preparation and evaluations are described in this section.

### Fluids

The brines were prepared by dissolution of the desired salts in deionized water in a volumetric flask. All the brine solutions were filtered through a 0.2- $\mu$ m cellulose acetate filter and the compositions are described in **Table 1** below.

*Table 1 Injection Brine Compositions*

Salt Type	Synthetic Injection Brine 1 (mg/L)	Synthetic Injection Brine 2 (mg/L)
NaCl	32,636	22,534
KCl	166	734
CaCl <sub>2</sub> .2H <sub>2</sub> O	4,306	1,100
MgCl <sub>2</sub> .2H <sub>2</sub> O	2,651	7,026
BaCl <sub>2</sub> .2H <sub>2</sub> O	59.2	-
SrCl <sub>2</sub> .2H <sub>2</sub> O	217.9	-
NaHCO <sub>3</sub>	103	-
Na <sub>2</sub> CO <sub>3</sub>	6	-
Na <sub>2</sub> SO <sub>4</sub>	136	3,512
Total Dissolved Solids, mg/L	37,915	30,898
R+	0.086	0.094

The polymers used in this study are commercial powders selected from SNF product lines including:

- Partially hydrolyzed polyacrylamide (HPAM)
- Partially sulfonated polyacrylamide (SPAM)
- Terpolymers containing sulfonated acrylamide (HSPAM)

All these polymers are produced using standard industrial polymerization techniques.

The characteristics of the 11 polymer samples evaluated in this study are summarized in **Table 2** below, with the weighted-average molecular weight of these polymers ranging from 9 to 27 MDa.

**Table 2** Polymer Properties Used as Part of This Study

ID	Chemistry	Range of Mw (x 10 <sup>6</sup> ) Da	ATBS Content	Total Anionicity
HPAM 1	AMD/AA	9-10	-	20-30 mol%
HPAM 2	AMD/AA	11-13	-	20-30 mol%
HPAM 3	AMD/AA	18-20	-	20-30 mol%
HPAM 4	AMD/AA	26-28	-	30-40 mol%
HSPAM 1	AMD/AA/ATBS	22-24	Low	30-40 mol%
HSPAM 2	AMD/AA/ATBS	18-20	Low	20-30 mol%
HSPAM 3	AMD/AA/ATBS	18-20	Medium	20-30 mol%
SPAM 1	AMD/ATBS	14-16	Med. High	20-30 mol%
SPAM 2	AMD/ATBS	7-9	High	30-40 mol%
SPAM 3	AMD/ATBS	8-10	High	30-40 mol%
SPAM 4	AMD/ATBS	13-15	High	30-40 mol%

A mother solution of 5,000 ppm was prepared by dissolution of the appropriate amount of polymer powder in the brine using a paddle stirrer set at 500 rpm. The brine was placed in a beaker and stirred at 500 rpm until a stable vortex is formed. The powder was then gently tapped into the wall of the vortex and the solution was left to stir for 2 hours and then mixed overnight at 150 rpm to complete the polymer hydration process. The solutions used for the coreflood injections were obtained by dilution of the 5,000 ppm mother solutions to the desired concentration (generally 1,000 to 2,000 ppm). All the polymer solutions were filtered prior to injection using 1.0- $\mu$ m polycarbonate filters.

The viscosity of the polymer solutions used in this study were measured using a Malvern Kinexus™ Pro+ rheometer. The rheometer was equipped with a cone and plate geometry having a 60-mm diameter cone with an angle of 2°.

### Filter Ratio (FR) Evaluation

Polymer filtration properties were evaluated using the filter ratio (FR) test through a hydrophilic membrane. As part of the polymer screening experiments, a standard FR method was implemented which consists of filtering a polymer solution through a 1.0- $\mu$ m polycarbonate filter (90-mm in diameter) under a constant pressure of 1 bar using nitrogen gas (Levitt and Pope, 2008). The filter ratio is defined accordingly in **Eq. (1)**:

$$FR (\text{Test 1, Test 2}) = \frac{t_{200\text{mL}} - t_{180\text{mL}}}{t_{100\text{mL}} - t_{80\text{mL}}} \quad \text{Equation 1}$$

Where  $t_{x\text{mL}}$  is the time required to collect X mL of filtrate (X being equal to 200, 180 or 100). Polymer solutions with  $FR < 1.2$  @ 1 micron were considered to be good quality for injection in low permeability porous media.

All the polymers for this study were characterized in terms of filterability under the following conditions

- FR Test 1: (P = 1 bar)
  - 1,000 ppm active concentration
  - 90-mm polycarbonate membrane with 1.0- $\mu$ m pore size
- FR Test 2: (P = 1 bar)
  - Target concentration to get 25 cP at 25 °C and 7.34 s<sup>-1</sup>
  - 90-mm polycarbonate membrane with 1.0- $\mu$ m pore size

## Evaluation of Polymer Transport in the Porous Media

A standard field-case, polymer-flow evaluation typically commences with coreflood experiments at 100% monophasic, water saturation either in representative cleaned outcrop rocks or sandpacks. These types of evaluations are often used to predict the polymer flow behaviour as a function of rock type and permeability, salinity and temperature conditions. Moreover, it is assumed that the experiments conducted without oil constitute the extreme case scenario where the retention of the polymer is typically the highest. Experiments can also be conducted to evaluate oil displacement, or to evaluate polymer flow behaviour at residual oil saturation (Sor) conditions. This study will focus on monophasic evaluations in consolidated cores, with an injectivity experiment conducted at Sor to provide some comparative discussion to the monophasic test results.

**Porous media.** (It should be noted that all permeabilities quoted in this study refer to absolute permeability to brine)

Representative outcrop rocks used in this study were purchased from Cleveland Quarries, Ohio. Sandstone outcrops of varying permeability and mineralogy used for the injectivity tests were chosen based on the relevant reservoir properties and mineralogy from ongoing customer projects globally. Berea outcrop sandstones have historically been used to represent oil-bearing reservoirs and two permeability ranges (mid-range and high) of similar mineralogy can be represented. Recently, a SNF internal market analyses suggested a significant increase in potential polymer flooding application for low permeability sandstones with high clay content. Therefore, the Bandera Grey and Brown outcrop rocks provided a heterogeneous, consolidated sandstone targeting the <20 mD permeability range. Detailed analysis using XRD and mercury injection capillary pressure (MICP) measurements were performed on each of these core samples to characterize core mineralogy and physical properties. The results obtained from core analyses are detailed in **Tables 3** and **4** and the pore throat distribution from MICP is illustrated in **Figure 1**.

**Table 3** Core Properties Used as Part of This Study

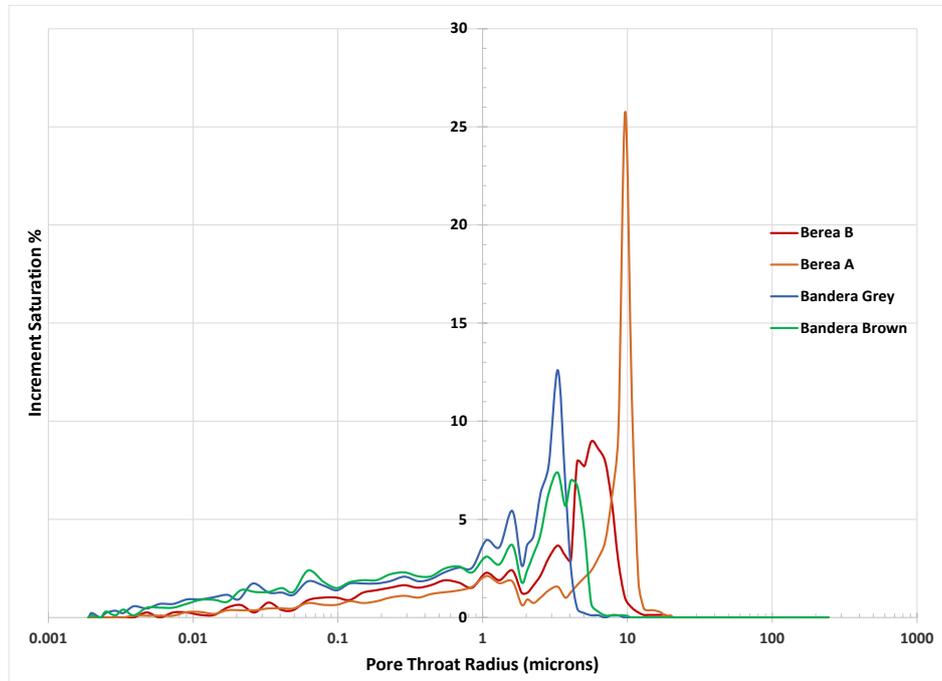
Core Type	Permeability range	Median Pore Throat Radius from MICP (µm)	Average Theoretical Pore Throat Radius (µm) using Equation 8
Berea A	110 to 220 mD	8.7	2.3
Berea B	30 to 60 mD	4.7	1.5
Bandera Brown	15 to 20 mD	2.2	0.8
Bandera Grey	5 to 10 mD	2.0	0.6

**Table 4** Mineralogy Composition of the Rocks from XRD Analysis

Core Type	Quartz	K-Feldspar	Plagioclase	Calcite	Dolomite	Kaolinite	Illite	Chlorite
Berea A	85.6	8.8	2.9	-	-	2.4	0.3	-
Berea B	84.2	7.1	3.6	3.6	0.9	3.4	0.8	-
Bandera Grey	69.7	-	20.7	-	1.3	4.5	3.1	0.7
Bandera Brown	70.7	-	20.2	1.7	-	2.9	3.2	1.3

Sandstones are classified as clastic rocks, which also includes conglomerates and shales. Unlike carbonates, the major components of sandstones do not dissolve in water, these being mainly stable minerals such as feldspar, quartz and rock fragments (Weimer and Tillman, 1982). Among other mineral components, high clay levels can lead to several problems during the lifetime of a petroleum reservoir (well-completion, drilling, waterflooding, etc), because of the sensitivity of clays to acid and salinity and migration of fine particles (Wang, 1990).

Clay minerals found in sandstones reservoirs are mainly classified as kaolinite, illite and chlorite, as shown in **Table 4**. Low exchange capacity clays can result in separation of clay platelets and migration during fluid flow causing serious damage to the formation. It is well established that the presence of clays is a critical factor in Chemical EOR projects and that the adsorption of polymers and surfactants in polymer flood and ASP projects increases with the quantity of clays (Chaudhuri, 2014).



**Figure 1** Pore Throat Distribution of Rock Samples from MICP Analysis

**Mobility ratio.** The mobility ratio is generally used to describe the efficiency of a displacement process such as waterflooding or polymer flooding. In the case of an oil/water system it is defined as follow:

$$M = \frac{K_{rw} \mu_o}{\mu_w K_{ro}} \quad \text{Equation 2}$$

Where  $K_{rw}$  and  $K_{ro}$  are the relative permeability of the water and oil respectively,  $\mu_w$  and  $\mu_o$  are the viscosity of the water and the oil phase respectively.

Pye (1964) published results on the properties of hydrolyzed polyacrylamides, specifically noting the difference between bulk solution viscosities compared to apparent viscosity of flowing solutions in porous media, or resistance factor (RF). This ultimately provides a unitless comparison of in-situ resistance for a given polymer solution to that of brine in the same porous media, pressure and temperature conditions. The resistance factor (RF) and residual resistance factor (RRF) are parameters which refer to the mobility ratio of the injected fluid and are typically used to describe the flow behavior of a polymer solution through the porous media. They are represented using the following definitions which can be reduced to simply the ratios between the pressure drops during polymer and brine flow, measured in the core at constant injection rates.

$$RF = \frac{\Delta P(\text{polymer flood})}{\Delta P(\text{brine before polymer flood})} \quad \text{Equation 3}$$

$$RRF = \frac{\Delta P(\text{brine after polymer flood})}{\Delta P(\text{brine before polymer flood})} \quad \text{Equation 4}$$

**Adsorption/retention.** The retention of polymer in porous media has a direct impact on its propagation in a reservoir and hence on its efficiency to displace and recover oil. Following this statement, a polymer with high retention will lead to an increased amount of polymer required to achieve target pore volume injected and cause significant delay in the production response. If insufficient polymer is ultimately injected, the anticipated recovery factor may not be fully realized. Green and Willhite (1998) illustrated this concept by studying the impact of the retention on the pore volume delay factor, representative of the breakthrough time. They reported that for a 1500-ppm polymer with a moderate retention of 100 µg/g, a delay of 35% was observed, compared to a polymer solution having no retention. This essentially means that 35% of additional polymer pore volume must be injected to reach the targeted in-situ concentration and volume of polymer required to overcome loss due to retention and provide sufficient sweep efficiency to maximize oil production, and thus it can directly affect the economics of polymer flooding projects. Zaitoun and Kohler (1987) investigated the role retention plays in polymer transport, systematically evaluating the conditions at which retention became worse and impacted polymer propagation through porous media. Five separate mechanisms controlling polymer transport were suggested: namely, i) inaccessible pore volume, ii) depletion layer effect, iii) irreversible adsorption, iv) hydrodynamic retention, and v) mechanical entrapment/bridging.

For the scope of this study, the polymer retention in different outcrops was measured using an in-line capillary viscometer at the outlet of the core using the double-bank method (Lotsch et al., 1985). The method includes injection of a first slug of polymer, followed by a brine flush to remove residual polymer, before injecting a second front of the same polymer slug (Zhang and Seright, 2013). The retention is calculated based on the difference in breakthrough volume between the two polymer fronts using the following equation:

$$\Gamma = \frac{V_{pol. front 1} - V_{pol. front 2}}{m_{dry}} \times C \quad \text{Equation 5}$$

Where  $V_{pol. front 1}$  and  $V_{pol. front 2}$  are the volume of polymer injected during 1<sup>st</sup> and 2<sup>nd</sup> front, respectively, to reach 50% of the final viscosity;  $C$  is the initial concentration of polymer injected; and  $m_{dry}$  is the weight of the dry core.

**Polymer in-situ rheology.** Usually, the HPAM solutions used for polymer flooding projects are in the semi-dilute regime. Most of the existing projects were performed with solutions ranging from 500 to 2,000 ppm. The HPAM polymers selected for the scope of this study displayed two main behaviors while measuring the viscosity over a range of shear rates (1 to 800 s<sup>-1</sup>): (i) only shear-thinning or (ii) Newtonian plateau and shear-thinning.

When it comes to flow in porous media, the polymer coils encounter successive shearing events due to the different sizes and geometries of the pores leading to contraction and expansion of the coils (Skauge et al. 2016). Above a critical shear rate, HPAM polymers exhibit a shear-thickening behaviour in solution up to another critical shear-rate where the resistance drops rapidly due to mechanical degradation. The critical shear rates can be determined experimentally by varying the interstitial velocity in 1-D experiments. The set of injectivity experiments selected for this paper were performed with an interstitial velocity set at 2 ft/day.

$$v = \frac{Q}{S \times \phi} \quad \text{Equation 6}$$

Where  $v$  is the interstitial velocity in m/day,  $Q$  is the flowrate in m<sup>3</sup>/day and  $\phi$  the porosity in %. The in-situ rheology flow curves are presented as a mean of RF as function of the velocity. The velocity can be later converted in shear-rate by applying Chauveteau's equation derived from the capillary bundle model (Chauveteau, 1982):

$$\dot{\gamma} = \alpha_2 \frac{4 \times v}{r_p} \quad \text{Equation 7}$$

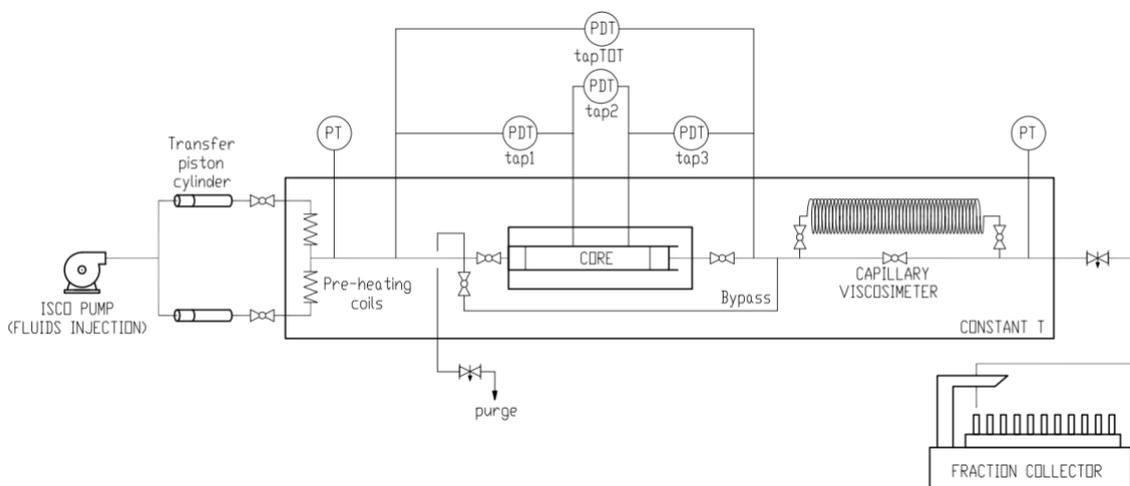
$$r_p = \sqrt{\frac{8 \times K}{\phi}} \quad \text{Equation 8}$$

Where  $\dot{\gamma}$  is the effective shear-rate in  $s^{-1}$ ,  $v$  the velocity in  $\mu m/s$ ,  $r_p$  the pore radius in  $\mu m$  (**Equation 7**) and  $\alpha_2$  a coefficient which relates to the geometry of the pores.  $\alpha_2$  was set on 2.5 for all of our experiments. The pore radius is theoretically calculated using **Equation 8**, where  $K$  is the absolute permeability in  $\mu m^2$  and  $\phi$  the porosity in %.

Polymer in-situ rheology studies provide additional information on comparative analyses of bulk rheological properties and in-situ behavior of polymer flow in the porous media, and can be used to:

- Determine the effect of polymer MW, ATBS content and absolute permeability on the resistance factor measurements during polymer flow in porous media
- Predict the mobility ratio of the polymer at near wellbore region (high shear rate) or deeper in the reservoir (low shear rates)

**Coreflood experimental protocol.** The experiments were performed using 1.5” diameter and 6” long outcrop rocks that were mounted in a coreholder provided by Phoenix Instruments. All the cores were vacuum saturated with the synthetic brines and absolute permeabilities measured by brine injection of at different flow rates. The first polymer slug was injected at 2 ft/D for approximately 5-20 PVs and steady state RF was estimated. Later, brine flush was performed for 25-30 PVs at 2 ft/D to estimate the RRF before injection of the second slug of the same polymer solution at 2 ft/D for another 4-6 PVs. The RF during the second slug was estimated, followed by in-situ rheology with varying polymer injection rates and estimation of the full RF vs interstitial velocity curve. The capillary inline viscometer was used to estimate polymer retention using the double bank method. The coreflood setup diagram is illustrated in **Figure 2**.



**Figure 2** Coreflood Setup Diagram used for polymer injectivity experiments

## Results & Discussion

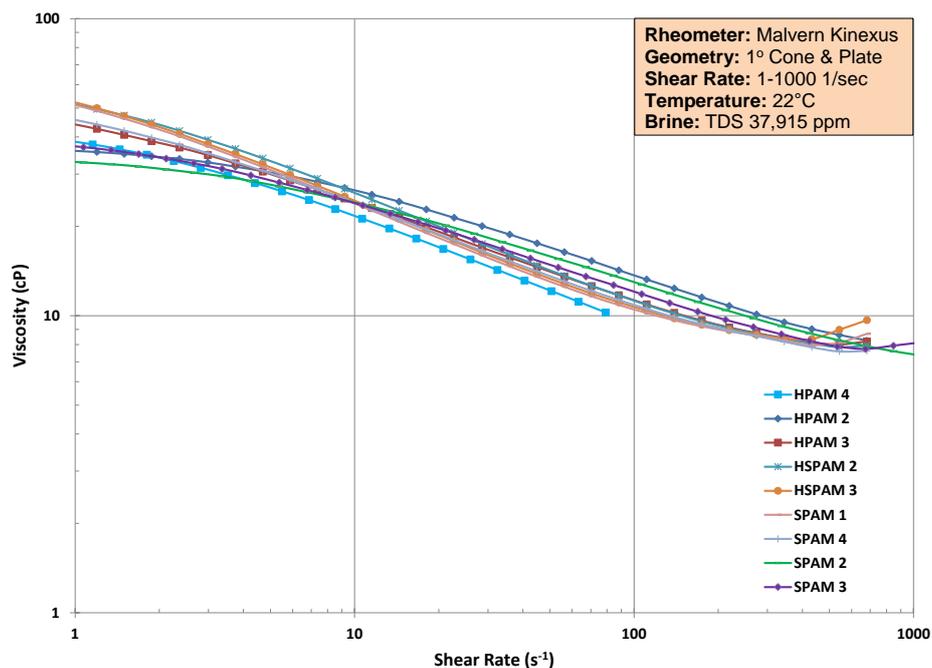
The assessment of polymer injectivity constraints were evaluated in sandstone outcrop rocks representing the following permeability ranges: (i) 100 to 200 mD, (ii) 40 to 80 mD and finally (iii) 5 to 20 mD. The preliminary step for polymer screening in EOR applications is to establish stable polymer transport properties in representative porous media. Hence, a systematic study was performed with different polymer chemistries along with varying MW as part of this work.

### Polymer Injectivity in Berea Outcrops (100-200 mD)

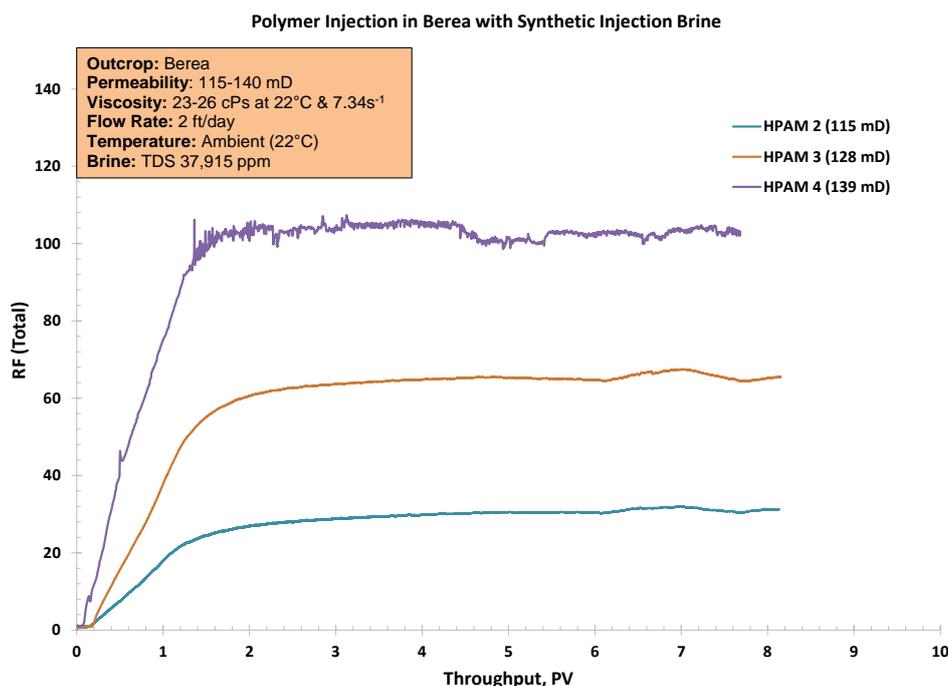
Synthetic Injection Brine 1 was used for this range of permeability tests and the polymers used included HPAMs with varying MW and ATBS content polymers to evaluate the transport properties of each of these polymer types. Each of these polymer injectivity experiments were performed with 25-cP polymer solutions measured at 22 °C and 7.34 s<sup>-1</sup>. The polymer shear viscosity sweep measurements are shown below in **Figure 3**. A few of the injected polymer solutions exhibited FR > 1.2 using FR Test 1 and were still considered for injection as part of this study.

**Figure 4** summarizes the polymer injectivity trends with HPAM 2, HPAM 3 and HPAM 4 polymers in Berea A outcrops at 2 ft/D injection rate (Darcy velocity). The results suggest successful transport for each of the polymers and with fast stabilization between 2-3 PV of polymer injection. Despite injection of similar shear viscosity solutions, higher MW polymers resulted in higher polymer in-situ resistance factor (RF) compared to smaller MW polymers, while retaining stable polymer injectivity. The polymer resistance factor for HPAM 4, increased by 4 times (RF = 104) and for HPAM 3 increased by 2 times (RF = 64) compared to HPAM 2 (RF = 27) in a similar permeability porous media. This polymer flow behaviour can be explained by comparative analysis of the average polymer size and the average pore throat size, as well as the pore throat distribution in the porous media as shown in **Figure 1**. To date, most of the available literature on polymer field injectivity have focused on HPAM 3 as the highest MW polymer in sandstone reservoirs (Kamal et al., 2015; Standnes et al., 2014; Guo, 2017). But with recent developments in polymer technology (raw materials, synthesis process etc.), HPAM polymers with 27-MDa or higher can be successfully injected in Berea outcrops of this permeability range.

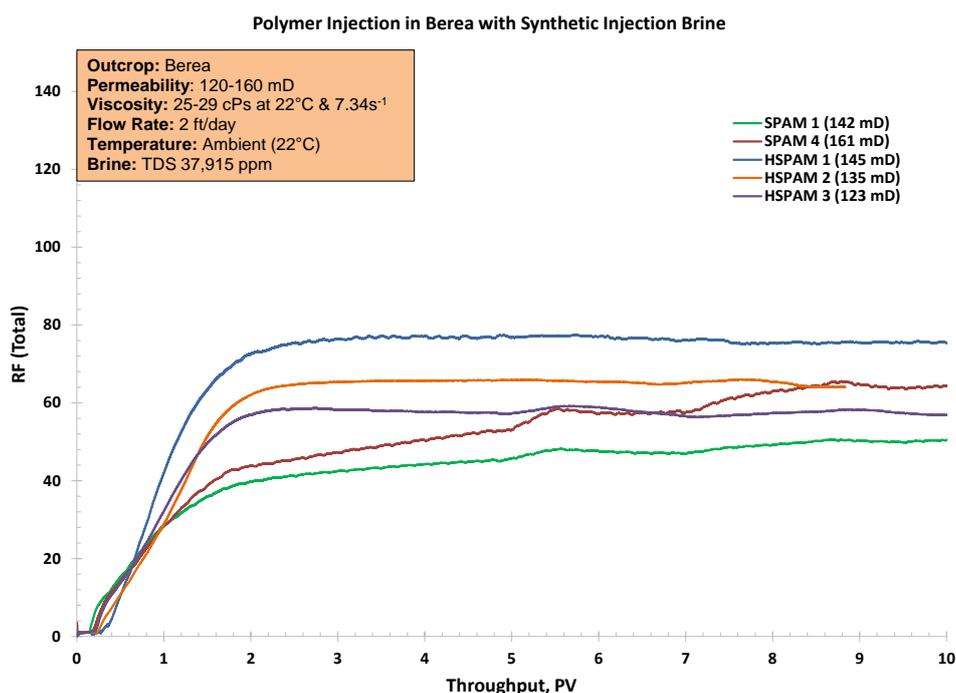
**Figure 5** summarizes the polymer injectivity trends with HSPAM 1, HSPAM 2, HSPAM 3, SPAM 1, and SPAM 4 polymers in Berea A outcrops at 2 ft/D injection rate. Each of these polymers contain varying amount of ATBS with approximate MW range of 18-25 MDa. The objective of this comparative study was to investigate the effect of changing ATBS level on polymer injectivity behavior in porous media. The results suggest similar injectivity behavior for HSPAM 2 (RF = 65) and HSPAM 3 (RF = 57), when RF is normalized with injected shear viscosity, while HSPAM 2 (RF = 76) exhibited slightly higher resistance due to its higher MW. On the other hand, HSPAM 1 with significantly higher MW and lower ATBS content showed the highest RF among these polymers. Polymer injectivity behaviour with SPAM 1 and SPAM 4 products in these Berea outcrops were non-ideal and showed gradual increase in RF over time; hence, results on the optimization study are described in the next section.



**Figure 3** Polymer Shear Viscosity Measurements in Synthetic Injection Brine 1 at 22 °C



**Figure 4** Single Phase Injectivity of HPAM polymers in Berea A outcrops at 22 °C

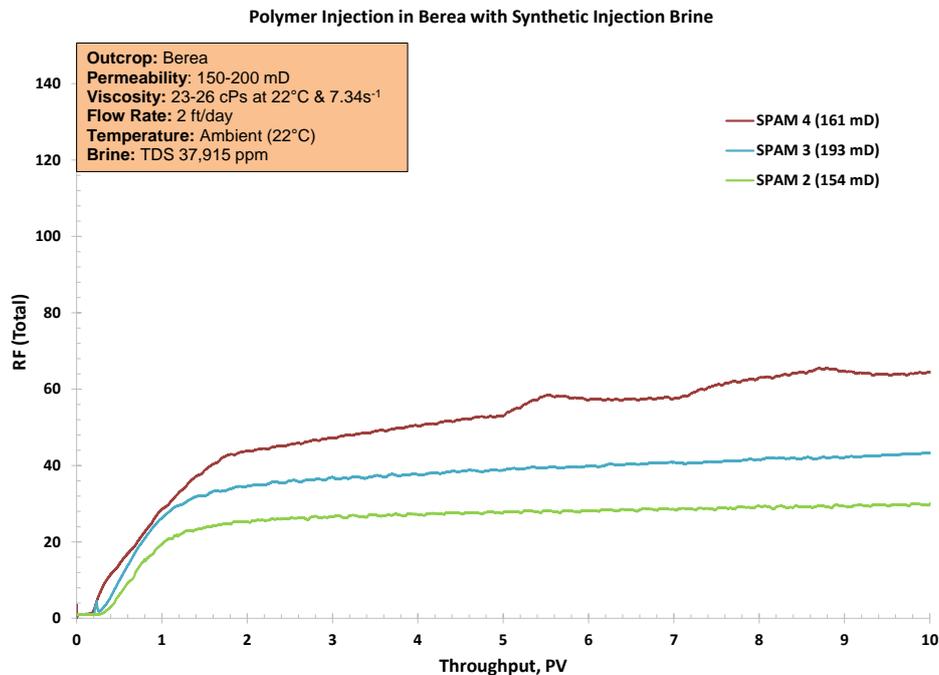


**Figure 5** Single Phase Injectivity of ATBS polymers in Berea A outcrops at 22 °C

**Selection of suitable polymer chemistry and MW for polymer injection**

The previous results with SPAM 4 showed gradual increase in RF over time, suggesting a polymer filtering effect at the smallest pore throats. As part of the optimization process, lower MW polymers with similar ATBS content were considered for this study. The results demonstrated significant improvement in polymer transport properties with slightly lower MW products (SPAM 2 and SPAM 3) compared to SPAM 4 in similar Berea outcrop cores, as shown in **Figure 6**. One of the key observations was the reduction in RF with reduction in MW, signifying the effect of MW on polymer transport behavior for similar chemistry products, with SPAM 2 displaying similar RF compared to injected shear

viscosity and higher MW polymers resulting in significantly higher RF values inside the porous media. The significance of polymer MW on steady state RF obtained during porous media flow can be attributed to the long, drawn-out trend representing the distribution of the smaller pore throats as observed in **Figure 1** for Berea A outcrops. As a result, detailed information on pore throat distribution rather than average pore throat size can be useful information to consider during polymer screening, as suggested by Ghosh et al. (2019). Hence, the results suggest that successful polymer injection with high level of ATBS can be achieved with careful choice of MW and ATBS level during polymer screening steps.



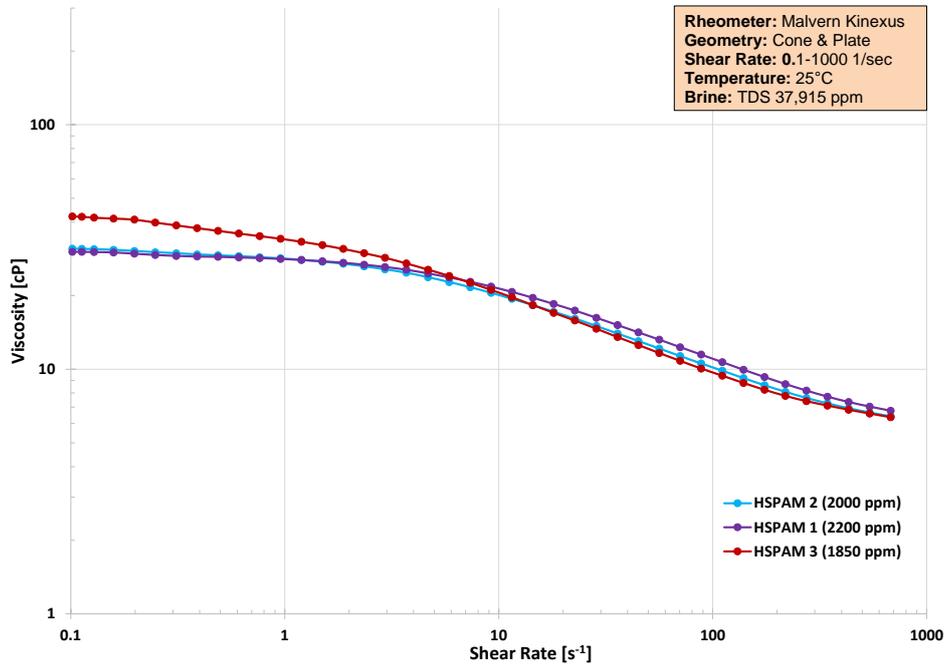
**Figure 6** Single Phase Injectivity of high-level ATBS polymers with varying MW in Berea A outcrops at 22 °C

### Polymer Injectivity in Low Permeability Berea Outcrops (40-80 mD)

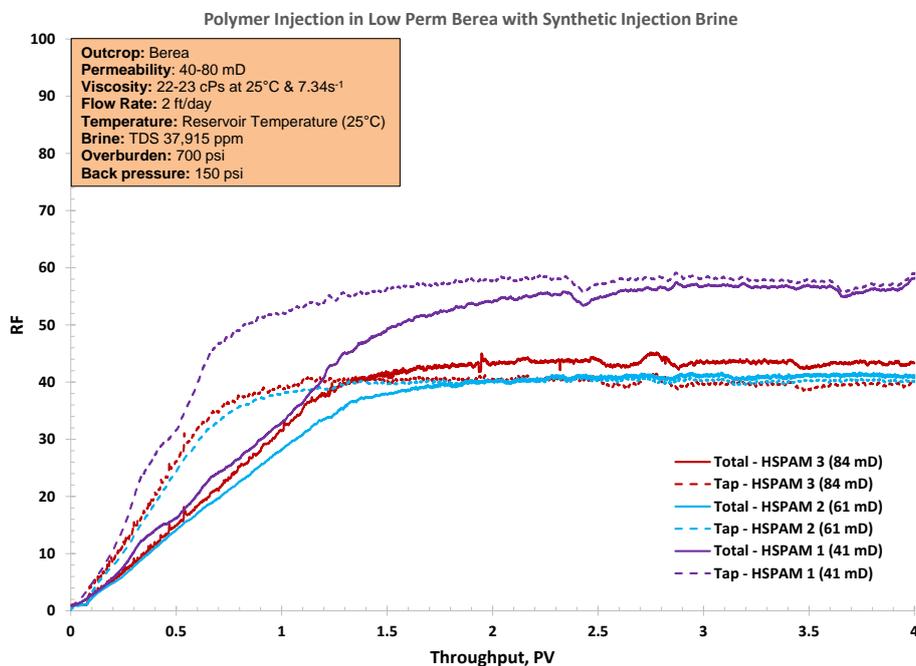
The results shown in the previous section suggested that in Berea A outcrops with a permeability range of 150-200 mD, due to improved synthesis process and product quality, polymers with 27 MDa MW can be successfully injected when low ATBS content is present. Hence, to provide further insight into improved polymer transport, a series of injectivity experiments were performed with Synthetic Injection Brine 1 in lower permeability Berea B outcrops. The focus here was to investigate the transport properties of ATBS polymers and find the injection constraints of high-level ATBS polymers, if any. Polymers used for this study were HSPAM 1, HSPAM 2 and HSPAM 3. Each of these polymer injectivity experiments were performed with 25-cP polymer solutions measured at 25 °C and  $7.34 \text{ s}^{-1}$ ; the polymer shear viscosity sweep measurements are shown below in **Figure 7**. Note, the polymer solutions injected in this section were pre-filtered using FR Test 2 (see Material and Methods section) to reduce any discrepancies of the effect of polymer solution quality on the repeatability of the injectivity behaviour.

**Figure 8** summarizes the polymer injectivity trends with HSPAM 1, HSPAM 2 and HSPAM 3 in low permeability Berea outcrops at 2 ft/D injection rate. Each of these polymers showed good propagation and fast stabilization around 1.5-2 PV of polymer injection. Both ATBS polymers HSPAM 2 (RF= 40) and HSPAM 3 (RF = 42) showed very similar injectivity behavior and steady state RF (approximately 2 times the injected viscosity) for similar injected viscosity solutions. Hence, varying level of ATBS did not show any marked difference on the injectivity behavior and the MW of the polymer predominantly determines the ultimate RF. This mechanism is further supported by the injectivity

behavior of HSPAM 1 with higher MW range that resulted in an RF value of 2.5 times the injected viscosity (RF = 54); although the injected viscosities for each of these polymer solutions were very similar. Note, on comparing the results from **Figures 8** and **4**, the differences in steady state RF for each of these polymers in low permeability Berea B (40-80 mD) and Berea A (100-200 mD) are largely due to the injection of pre-filtered and non-filtered solutions, respectively.



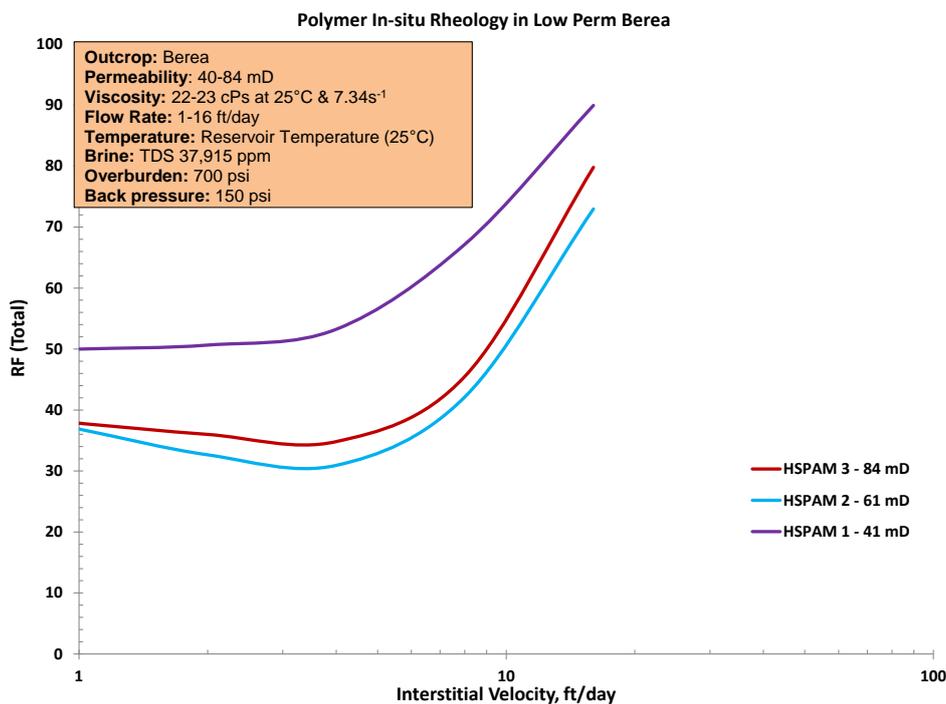
**Figure 7** Polymer Shear Viscosity Measurements in Synthetic Injection Brine 1 at 25 °C



**Figure 8** Single Phase Injectivity of ATBS polymers in low permeability Berea B outcrops at 25 °C

In addition, full characterization of polymer flow behaviour was also performed as part of this study to understand the in-situ polymer rheology: RF, RRF and polymer retention based on the polymer chemistry and MW. The polymer retention was measured using the double bank method (Lotsch et al., 1985; Zaitoun and Kohler, 1987), with the same polymer slug injected at 2 ft/D with an exhaustive brine

flush in between. The calculated polymer retentions for HSPAM 1, HSPAM 2 and HSPAM 3 were 78.4, 80.9 and 40.3  $\mu\text{g/gm}$  of rock, respectively. These values are consistent with other studies on low permeability porous media in the range of 5-140 mD (Vela et al., 1974; Zitha et al., 1995, 1998, 2001; Castagno et al., 1987; Zhang and Seright, 2013; Al-Shakry et al., 2019; Guetni et al., 2019). The RRF values measured after 25 PV of brine flush at 1 ft/D for HSPAM 1, HSPAM 2 and HSPAM 3 were 28.3, 22.0 and 25.5, respectively. These high RRF measurements can be attributed to the high MW polymers injected in low permeability porous media and unfavourable mobility ratio during the brine flush, which could be reduced significantly by higher volume of brine injection (50+ PVs of brine) (Seright, 2016). Zaitoun and Chauveteau (1998) reported similar observations in low permeability heterogeneous porous media which resulted in high RRF estimation due to slower polymer unbridging effect. Polymer in-situ rheology was performed by varying rates from 16 to 1 ft/D at the end of second polymer slug injection to investigate the effect of different flow regimes of the polymer on resistance factor estimation. The in-situ rheology for each of these polymers are described in **Figure 9**. In addition, the higher MW products have earlier on set of the shear thickening regime, which can be further accelerated by lower permeability porous media, as reported earlier by several researchers (Seright et al., 2010b; Zitha et al., 1998; Al-Shakry et al., 2019). The results suggested that the highest MW polymer HSPAM 1 has the most shear-thickening behaviour and the on-set of the shear-thickening regime also occurred the earliest, at around 3 ft/D. On the other hand, both HSPAM 2 and HSPAM 3 showed similar injectivity trends and similar on-set of the shear-thickening regime observed at 4 ft/D. This was attributed to the similar MWs for the two polymers, with the exception that the lower ATBS content polymer appeared to be more susceptible to higher shearing at higher flow rates and compete against the rate of increase in RF at higher flow rates in presence of possible drag reduction effect. Hence, the above results provide valuable information on the flow behavior of polymer near wellbore (high flow rates), as well as deep into the reservoir and can be useful for design considerations and field implementation of any polymer flooding project.

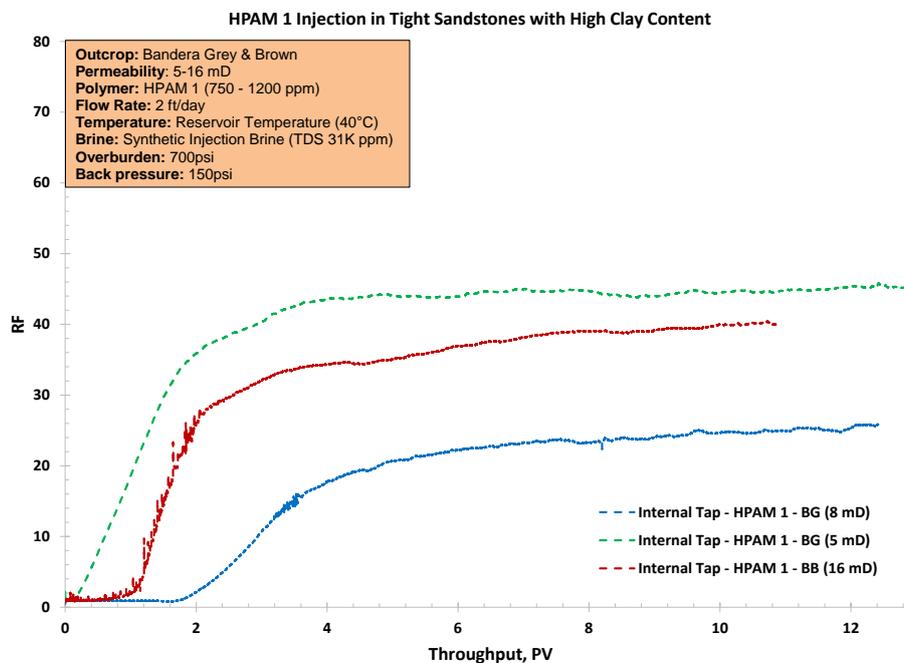


**Figure 9** In-situ rheology for ATBS polymers in low permeability Berea B outcrops at 25 °C

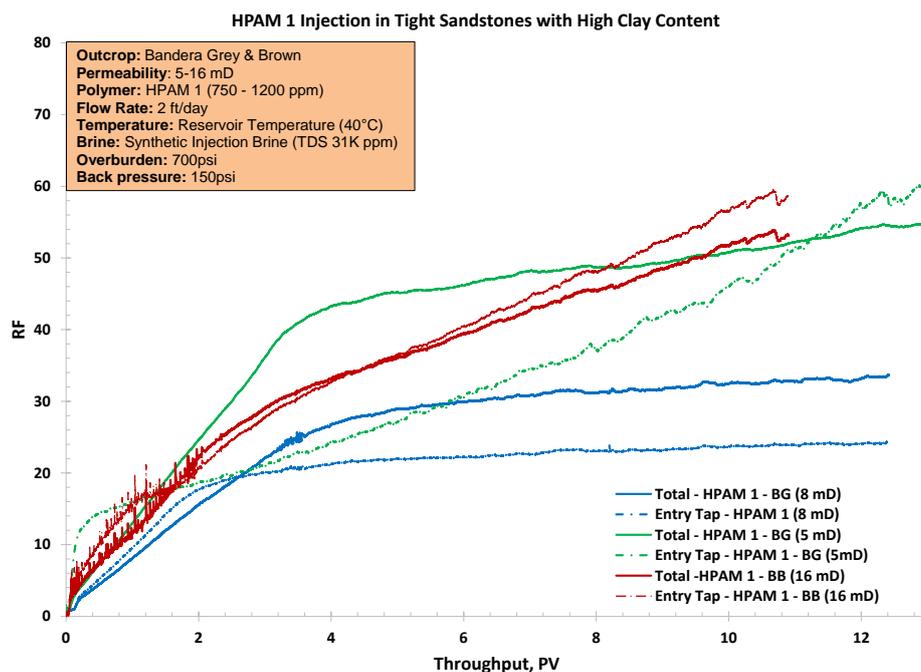
### Polymer Injectivity in Tight Sandstone Outcrops Containing Clays (5-20 mD)

The results have so far demonstrated the successful propagation and transport of high MW polymers containing moderate ATBS levels, which seems to enhance the potential of implementing polymer

flooding in low permeability sandstones (e.g., 40-100 md). In order to push the boundaries of polymer flooding to even more challenging reservoir conditions, polymer injectivity experiments were performed in low permeability sandstones containing higher amounts of clay (7-9 wt.%). For this part of the study, Bandera Brown and Bandera Grey outcrops were used for the polymer injectivity experiments, and HPAM 1 polymer was prepared in Synthetic Injection Brine 2. Each of the polymer solutions were pre-filtered using FR Test 2 to ensure consistent solution quality before injection at the reservoir temperature (40 °C). The first set of experiments were performed in Bandera Grey outcrop rocks, utilizing 750-ppm and 1,200-ppm solutions of HPAM 1 to investigate the polymer injectivity profile at different polymer concentrations. The results suggested stable propagation for both polymer concentrations of 750 ppm (RF= 22) and 1,200 ppm (RF = 45), exhibiting almost 2 times increase in RF and faster stabilization after polymer breakthrough obtained at the higher concentration, as shown in **Figure 10**. The results suggest faster satisfaction of the polymer adsorption mechanism at higher polymer concentration. An additional injectivity experiment was performed with HPAM 1 (1,200 ppm) in Bandera Brown which suggested similar injectivity profile with significant increase in RF compared to injected viscosity of the polymer solution. Note, that the total and entry tap RF profiles show gradual increase in some of the experiments; these were attributed to entry effects believed to be caused during the core drilling process, as illustrated in **Figure 11**. Polymer retention, using double bank method, was measured in this experiment and the results are summarized in **Table 5** below. The results suggest that polymer entanglement in different concentration regimes can affect the polymer retention more significantly than mineralogy of porous media in such tight permeability formations. The high polymer retention measurements reported in tight sandstones with significant amount of clay are in agreement with the findings in 72-mD sandpacks of quartz and illite presented by Guetni et al. (2019) and Sandengen et al. (2017), which also found increased polymer adsorption in rocks containing clays. These results also suggest great potential of polymer flooding application in relatively low permeability sandstones (5-20 mD range) with higher clay content and can help in expanding the polymer EOR processes into these more challenging reservoir conditions previously considered not suitable for polymer flood. Further optimization is possible for polymer injectivity in these extreme conditions, however, careful selection of polymer chemistry and concentration can help reduce the RRFs and polymer retention, but unfortunately is not part of the scope of this study and will be considered in future work.



**Figure 10** Single Phase Injectivity of HPAM 1 polymer in Tight Sandstone Outcrops at 40 °C



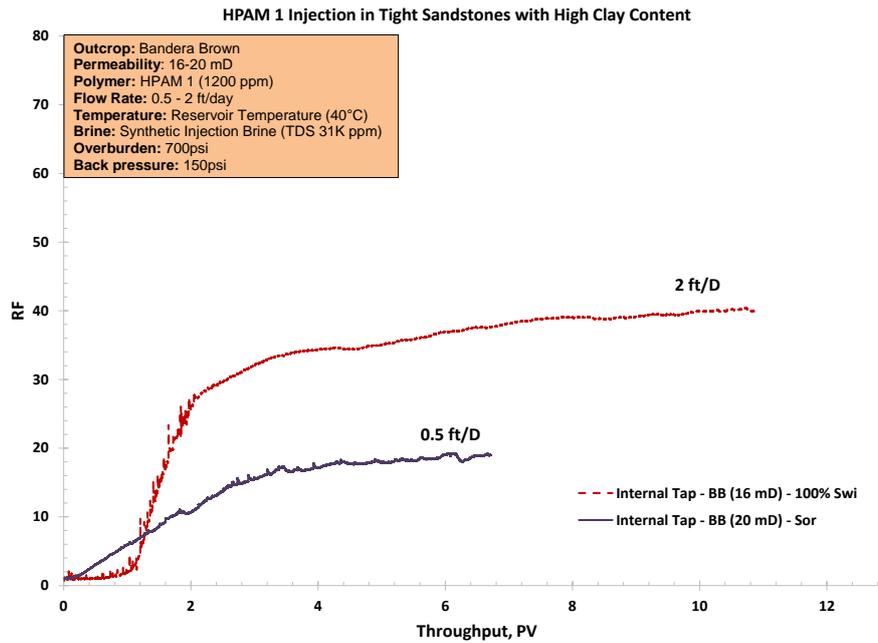
**Figure 11** Single Phase Injectivity of HPAM 1 polymer in Tight Sandstone Outcrops at 40 °C

**Table 5** Polymer Injectivity Results in Tight Sandstones at 40 °C

Polymer Name	Core Type	Polymer Concentration (ppm)	Polymer Retention (µg/gm)
HPAM 1	Bandera Grey (8 mD)	750	190.8
HPAM 1	Bandera Grey (5 mD)	1,200	262.2
HPAM 1	Bandera Brown (16 mD)	1,200	269.9

### Polymer Injectivity in Tight Sandstone Outcrops at Sor Conditions (5-20 mD)

An additional polymer injectivity experiment was performed in an aged (3 weeks), oil-wet Bandera Brown sandstone outcrop rock, utilizing HPAM 1 polymer to compare the polymer transport behaviour in presence and absence of crude oil in rocks with high clay content. A 27.6-cP, medium crude oil measured at 40 °C was used for this study. The initial oil saturation for the aged core was 59.5%. Waterflood was performed at 2-4 ft/D for 8 PVs followed by a viscosified brine mixture (glycerol + brine) to achieve residual oil saturation to water. A 1,200-ppm polymer solution of HPAM 1 was injected at 0.5 ft/D after an exhaustive brine flush to remove the in-situ viscosified brine solution. The polymer injectivity behaviour for the HPAM 1 in presence and absence of crude oil is illustrated in **Figure 12** for the internal pressure tap section. Note, the single phase injectivity with HPAM 1 in Bandera Brown was performed at 2 ft/D, described earlier in **Figure 10**, that resulted in almost 2 times higher RF compared to the steady state RF obtained in an aged, oil-wet core. The results suggest similar stabilization time for HPAM 1 in both injectivity experiments of approximately 4 PV. A more detailed understanding of polymer flow behaviour in presence of crude oil and comparative study of polymer flow physics in presence and absence of crude oil for different rock mineralogy will be investigated in a future publication; as the presence of residual can influence the flow behaviour of polymer solutions.



**Figure 12** Polymer Injectivity of HPAM 1 in Presence and Absence of Crude Oil in Bandera Brown at 40 °C

### Summary

The results obtained in this scope of work in different permeability range of the sandstone outcrops along with varying mineralogy have been summarized in **Table 6**. Steady state RF for a given polymer depends primarily on the MW range, rather than the chemistry of the polymer for a given porous. Polymer retention increases with decrease in permeability and increase in clay content, primarily due to increase in mechanical entrapment even with ranges of lower MW polymers.

**Table 6** Polymer Injectivity Results Summary in Sandstone Outcrops

	Polymer Name	Permeability (mD)	Mw range x 10 <sup>6</sup> Da	RF (@10 PV)	Polymer Retention (µg/gm)
<b>Berea A</b>	HPAM 2	115	11-13	28	40.1
	HPAM 3	128	18-20	63	63.2
	HPAM 4	139	26-28	100	83.0
	HSPAM 1	145	22-24	76	97.4
	HSPAM 2	135	18-20	64	-
	HSPAM 3	123	18-20	56	-
	SPAM 1	142	14-16	47	-
	SPAM 4	161	13-15	64	-
	SPAM 3	193	8-10	40	-
	SPAM 2	154	7-9	25	-
<b>Berea B</b>	HSPAM 1	41	22-24	55	78.4
	HSPAM 2	61	18-20	38	80.9
	HSPAM 3	84	18-20	40	40.3
<b>Bandera Grey</b>	HPAM 1	8	9-10	22	190.8
	HPAM 1	5	9-10	45	262.2
<b>Bandera Brown</b>	HPAM 1	16	9-10	37	269.9

## Conclusions

This study highlights the promising potential of polymer flooding application in relatively low permeability sandstone reservoirs (5-200 mD) and extends the lower constraint of reservoir permeability for possible polymer flooding candidates. Some of the key findings from this scope of work are the following:

- Contrary to existing literature on limits of polymer injectivity, recent improvements in polymer technology have allowed redefining the limit of injectivity in terms of MW of polymers and absolute permeability of porous media. Results showed successful injection of higher than 25 MDa MW polymers in 100-200 mD Berea outcrops at 100% water saturation.
- For Berea ~150-200 mD, post hydrolyzed polymers of MW range 28-30 MDa showed good propagation and fast stabilization and reasonable polymer retention was determined. Significantly higher resistance factor or in-situ apparent viscosity was measured, thus improving the mobility control in the porous media.
- For Berea ~150-200 mD, in high salinity and temperature conditions, careful selection of ATBS polymers and corresponding MW range is crucial for successful polymer injection. High MW polymers with high level of ATBS showed slow pressure build-up over time, but lower MW showed good propagation in similar porous media. This emphasizes the importance of proper polymer screening and optimization during laboratory evaluation studies, complemented with detailed core analysis for a suitable polymer candidate.
- For Berea ~40-60 mD, good polymer propagation was observed with high MW polymers and results suggested optimization of MW with increasing ATBS level for successful propagation. Similar polymers showed evidence of increase resistance factor and polymer retention in lower permeability Berea cores. The higher resistance factor in lower permeability cores can be beneficial in optimizing polymer dosage during polymer flooding.
- For tight, low permeability sandstones (<20 mD) with higher clay content (7-9%), successful injection of HPAM 1 (9-10 million Da Mw, 20-30% anionicity) was observed with significantly higher resistance factor and polymer retention. Higher stabilization time of the polymer bank was observed in these outcrop rocks due to higher polymer adsorption stabilization time. Hence, polymer choice (possibly a lower MW) and optimization is necessary for successful implementation of polymer flooding in these challenging reservoir conditions.

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## Abbreviations

ATBS - acrylamide tertiary butyl sulfonic acid  
FR – filter ratio  
MICP – mercury injection capillary pressure  
MW - molecular weight (MDa)  
HPAM – partially hydrolyzed polyacrylamide  
HSPAM – ter-polymers containing sulfonated acrylamide  
Kro – relative permeability to oil  
Krw – relative permeability to water  
PAM – polyacrylamide  
RF – resistance factor  
RRF – residual resistance factor  
Rp - pore throat radius ( $\mu\text{m}$ )  
SiC – silicon carbide  
Sor – residual oil saturation

SPAM – partially sulfonate polyacrylamides

$V_{\text{pol}}$  – volume of polymer injected (mL)

$\Delta P$  – pressure drop (psi)

$\Gamma$  – adsorption ( $\mu\text{g/g}$ )

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