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POLYMER FLOODING IN SANDSTONE: ADSORPTION AND OIL DISPLACEMENT

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Abstract. *The addition of polymers to the injection water is one of the most used enhanced oil recovery (EOR) methods because of the ability of these compounds to increase the viscosity of the solution even at low concentrations. This increase of the water phase viscosity promotes the reduction of the mobility ratio between fluids, improving the displacement of oil. However, there is a large number of factors related to the use of these substances that can modify the original characteristics of the porous medium. In order to better understand these mechanisms, a review of the characteristics related to polymer flooding, and an experimental analysis were carried out to verify polymer adsorption mechanism and oil recovery processes. Three types of core samples with different petrophysical characteristics were used. Tests were carried out to study polymer adsorption on formations under specific working conditions using the Two Slug Method. Then, oil recovery tests were performed with the injection of different water phases: sea water, polymer solution and glycerol-water solution with the same viscosity of the polymer solution. Results showed the efficiency of the Two Slug Method in adsorption tests and the use of polymer solutions in oil recovery processes.*

Keywords: *Polymer Solutions, Enhanced Oil Recovery, Adsorption, Retention, Sandstones.*

1. INTRODUCTION

Water injection is one of the most used oil recovery methods in the industry due to its simplicity and low cost operation. However, the volume of oil that remains in reservoir is significantly large. Advanced recovery methods have emerged as an attempt to optimize oil recovery processes (Rosa, 2006).

The use of polymer additives in the flood water as an enhanced oil recovery method has been growing in recent years due to the better fundamental and practical knowledge of the process. The injection of polymer solution improves the mobility ratio between water and oil phases, resulting in a better oil displacement and consequently an uniform swept. Although polymer solutions have been used in advanced stages of reservoir production, this work proposed a study of the application of this technique on earlier stages. According to Standnes and Skjevrak (2014) polymer injection in secondary mode shows a higher success rate than in tertiary mode.

Despite the tremendous benefits that polymer injection attains in oil recovery, it is well known that formation damage (reduction of rock permeability) and injectivity loss are important drawbacks resulting from polymer retention, because of that, this technique has been extensively studied in laboratory and field tests. There are two main types of polymer retention in porous medium: mechanical trapping and adsorption. Mechanical entrapment is a function of pore size distribution and is more likely to occur in low permeability formations (Szabo, 1975). It usually occurs when polymer molecules become trapped in channels of the porous media (Willhite & Dominguez, 1977). Polymer adsorption is caused by the interaction between polymer molecules and solid surface, and also by physical adsorption, Van der Waals force and hydrogen bond (Sheng, 2011). In order to better understand these mechanisms, a review of the characteristics related to polymer flooding, and an experimental analysis were carried out to verify polymer adsorption mechanism and its consequences in oil recovery processes.

Laboratory flooding experiments were conducted with the most widely used synthetic polymer in EOR applications, polyacrylamide (PAM) in its partially hydrolyzed form (HPAM). HPAM is a synthetic straight-chain polymer of acrylamide monomers, some of which have been hydrolyzed. The degree of hydrolysis controls some physical properties such as polymer stability and adsorption (Sorbie, 1991). Hydrolysis converts some of amine groups ($CONH_2$) to carboxyl groups (COO^-) reducing the attraction of polymer chains to certain types of minerals on the porous medium walls (Sheng, 2011). Besides hydrolysis, many other factors have a huge influence on polymer retention, such as: rock surface, permeability, salinity, molecular weight, temperature and polymer concentration.

In this work, the effect of some of the factors listed above were noticed and studied. There will be some citations of Peregrino oil filed during this document, but experiments have no relationship to this specific area.

2. EXPERIMENTAL PROCEDURE

The effect of polymer solution injection through a porous medium was experimentally studied on a core flooding system, using the rig setup described on Fig. 1. Three types of sandstone core samples, with different mineralogical and petrophysical characteristics were used in three different procedures: polymer adsorption tests and two oil displacement protocols. The temperature of all tests was 40°C. The confining and pore pressure used were 1500 PSI and 70 PSI, respectively.

2.1 Materials

Core Material

The sandstone cores used were Buff Berea, Gray Berea and Bentheimer. These rocks were chosen due to their diversity on mineralogy and permeability. As mentioned before, these two properties may influence on polymer retention. The presence of certain types of minerals such as clay and calcium carbonate increases the interaction between the surface and carboxylate groups on the HPAM (Smith, 1970; Szabo, 1979, Lakotos *et al*. 1979). Rocks with low permeability promotes mechanical entrapment increasing polymer retention (Sheng, 2011). To better understand these factors, cores with different permeability and clay content were used. Their mineralogical composition are given in Tab. 1.

Table 1 - Mineralogical composition of sandstone core samples (Kocurek Industries INC).

Gray Berea		Buff Berea		Bentheimer	
Silica	93.13%	Quartz (SiO2)	83%	Quartz (SiO2)	95%
Alumina	3.86%	Plagioclase Feldspar	1%	Plagioclase Feldspar	trace
Ferric Oxide	0.11%	Potassium Feldspar	2%	Potassium Feldspar	2%
Ferrous Oxide	0.54%	Kaolinite	4%	Kaolinite	2%
Magnesium Oxide	0.25%	Chlorite	trace	Chlorite	nd
Calcium Oxide	0.10%	Mika and/or Illite	nd	Mika and/or Illite	trace
Loss on Ignition	1.43%	Mixed-Layer Illite>95/Smectite<5	10%	Mixed-Layer Illite>95/Smectite<5	nd

Fluids

Three water phases were used: (1) a brine that mimics the composition of a high salinity oil field case “Peregrino-water”, (2) HPAM AN125VHM polymer solution and (3) glycerol-water solution with the same viscosity of polymer solution. The mineral oil used in this study was AGECOM 500PS. The composition of the synthetic brine as well as the properties of the fluids used are given in Tab. 2 and Tab. 3.

Table 2 - Composition of synthetic brine (Peregrino-water).

Salt	Concentration (g/L)	Unhydrated Salts (g/L)	mmol/L
NaCl	86.6	88.60	1481.86
$CaCl_2$*2H2O	10.0	7.55	68.02
$MgCl_2$*6H2O	6.3	2.95	30.99
KCl	0.6	0.60	8.05
Na_2SO_4	1.3	1.30	9.15
TDS	99000 g/L		

Table 3 - Fluids Properties @ 40°C.

Fluid	Density (g/cm3)	Kinematics Viscosity (mm^2/s)	Dynamic Viscosity (cP)
Brine 70%	1.0374	0.7389	0.766
AGECOM 500PS	0.8725	92.7537	80.9286

After preparation, part of the brine was diluted to 70% of its original concentration and part was used to prepare the polymer solution. This salinity/conductivity difference was used as water tracer.

Solutions of AN125VHM were prepared according to the "Recommended Practices for Evaluation of Polymers Used in Enhanced Oil Recovery Operations" (API RP*63, 1990). The powder was uniformly sprinkled in the vortex created by stirring the synthetic brine to produce a stock solution of 5000 ppm. After that, this solution was diluted to 1000 ppm and filtered. The filtration protocol states that a 1.0 g/L solution must be pumped through a 5-micron filter membrane with a differential pressure of two bars. Finally, solutions were placed inside a glove bag and bubbled with an inert gas (Argon) to reduce the concentration of dissolved oxygen in order to avoid polymer degradation.

Glycerol-water solutions were prepared to achieve an equivalent viscosity of polymer solutions for each test. The reason to use this solution was to isolate the oil displacement caused by polymer retention, since glycerol-water solution could not be retained on porous media. Preparation was done by following a specific procedure involving (a) determination of test core permeability and porosity, (b) estimation of shear rate of solution in the porous media using Christopher & Middleman (1965) mathematical model, (c) dilution of glycerol in brine, and finally (d) solution filtration and inert gas injection.

Experimental Setup

In this work, two different rig setups were used, on for the adsorption test and another to oil displacement test. The setup was equipped with two constant flow pumps Waters 515 HPLC, three 500 ml cylindrical accumulators in which fluids were stored, two thermosetting loops upstream the core holder to ensure that fluids entered the porous medium at test temperature, a core-holder for the filter core and another core-holder for test core. Downstream the porous medium were a conductimeter and a system of capillary tubes, to determine fluids interface and solutions viscosities, respectively.

All parts contacted by solutions that were inside the oven were made of non-metallic material to avoid oxidation and consequentially solution degradation. Fig. 1 shows the rig setup used on adsorption tests. A Bentheimer filter core was placed upstream of the test core to ensure that polymer solution entered test core free of lumps. For oil displacement tests the core filter was removed and solutions were injected directly on test core. The measurement system located downstream the core-holder were removed as well.

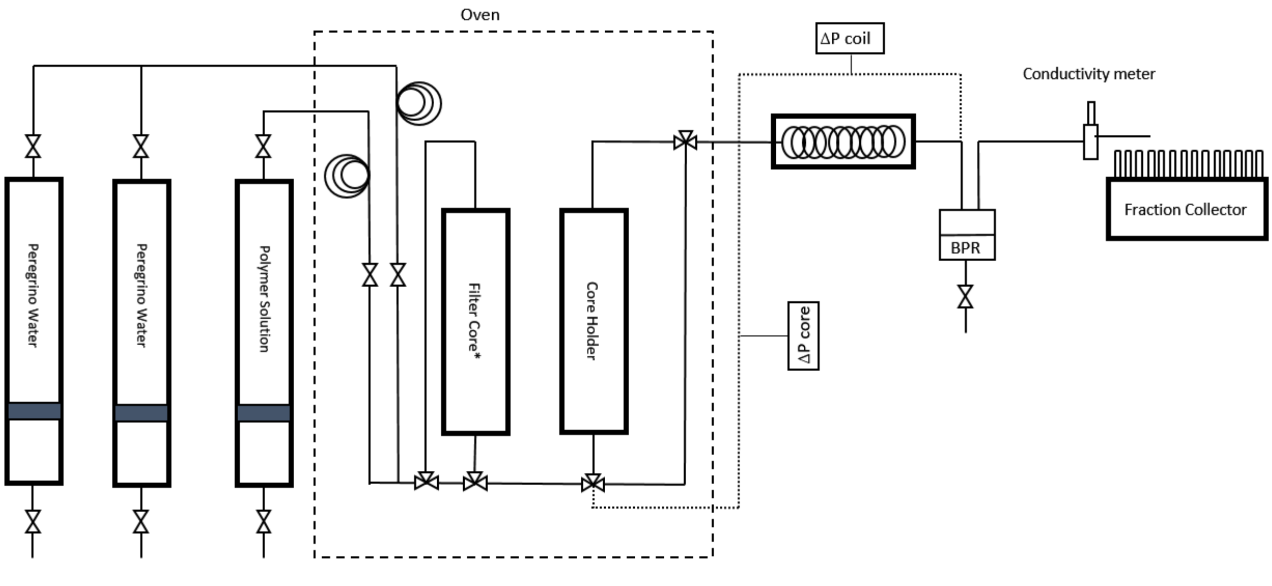

Figure 1. Experimental setup (Core Flooding System).

2.2 Polymer Adsorption

Polymer adsorption is considered an irreversible process in most of the cases. The effect of polymer injection on porous medium walls may be estimated by quantifying the polymer mass irreversibly adsorbed, inaccessible pore volume, resistance factor and residual resistance factor.

Tests were carried out using the "two slug" method, described on Fig. 2. This method was used by Lotsch in 1985 to study the effect of inaccessible pore volume on polymer core flood experiments and it consists of two polymer slugs interposed by a waterflooding. The first polymer slug is injected until the stabilization of ΔP along the core. Then, waterflooding is performed to rinse the core by carrying all non-absorbed polymer from porous medium. Finally, the second polymer slug is injected until ΔP core become stabilized again.

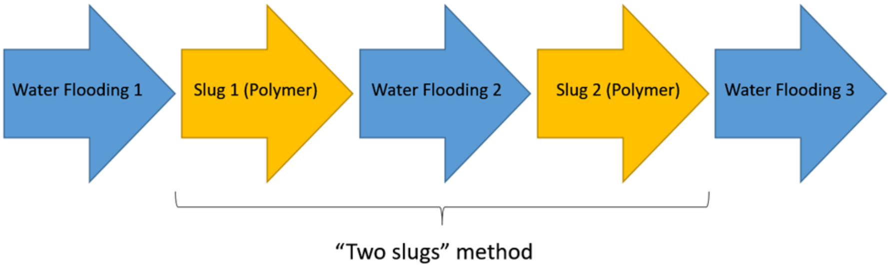

Figure 2. "Two slug" method sequence.

As mentioned before, polymer effluent concentration and conductivity was measured by ΔP across a capillary tube and by a conductimeter, respectively. These readings generate polymer and tracer breakthrough curves as function of injected pore volume, as showed in Fig. 3. The difference in pore volume between slug 1 and 2 (at the inflection point) gives the volume of polymer solution corresponding of the mass of polymer irreversibly adsorbed, and the difference between conductivity and slug 2 (at the inflection point) gives the inaccessible pore volume. Equation (1) describes the mass of polymer adsorbed, where V_{ads} is the volume of polymer solution corresponding of the mass of polymer irreversibly adsorbed on the pore walls, C_{pol} is the polymer mass concentration and m_{rock} is the mass of solid in the porous medium.

The permeability reduction is one of the main consequences of polymer adsorption on formation walls. The initial and final permeability of test core are determined before and after the injection of the two slugs, respectively. The resistance factor (RF) and the residual resistance factor (RRF) can be determined by the steady state pressure difference of the initial water flow, the polymer injection and the water flow after the polymer injection. RF and RRF are described in Eq. 2 and Eq. 3, where λ is the mobility, k_r is the relative permeability, μ is the dynamic viscosity of water ($_w$) and polymer ($_p$), and phases 1 and 2.

$$\tau = (V_{ads} \,.\, C_{pol}) / m_{rock} \tag{1}$$

$$RF = \lambda_w / \lambda_p = (k_{rw} / \mu_\omega)(\mu_p / k_{rp}) \tag{2}$$

$$RRF = \lambda_{w1} / \lambda_{w2} = (k_{rw1} / \mu_{\omega 1})(\mu_{w2} / k_{rw2}) = k_{rw1} / k_{rw2} \tag{3}$$

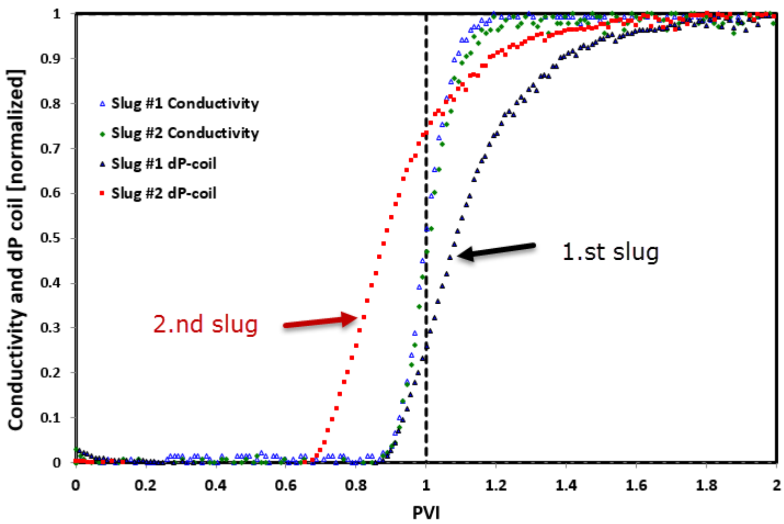

Figure 3. Polymer and tracer (conductivity) breakthrough curves (Sandengen *et al.*, 2017).

2.3 Oil Recovery – Protocol 1

The first oil recovery protocol was performed with three different methodologies that result in a total of 9 phases, as described in Fig. 4.

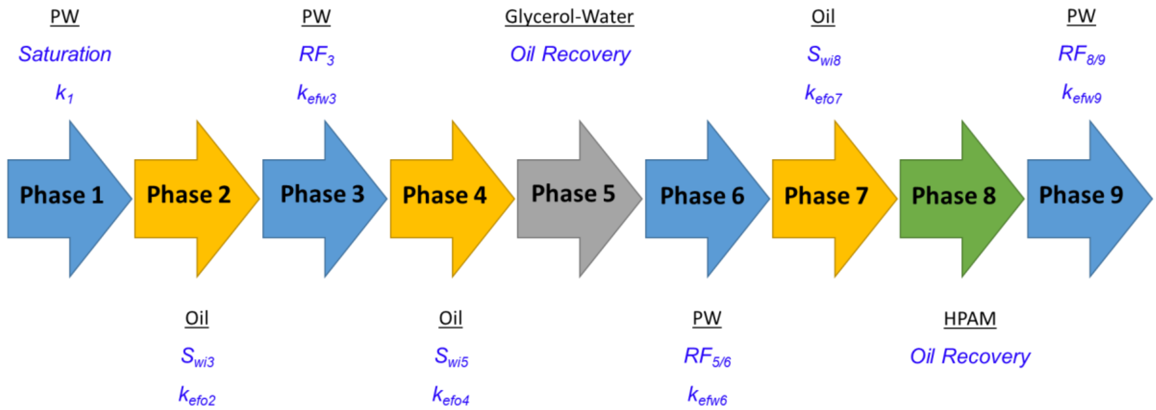

Figure 4. Schematics of oil recovery protocol 1.

As illustrated in Fig. 4, protocol 1 used three different oil recovery methods: water, glycerol-water solution and polymer solution. Afterwards each oil recovery process, the core test was saturated with oil again in order to establish the new conditions for the next recovery procedure.

After the glycerol-water solution injection in protocol 1, it was noted that the differential pressure profile across the core sample was above the regular values for rocks with low permeability, as shown in Fig. 6 and Fig. 7, so it was decided to run a new test without the phases related to glycerol-water solution (Protocol 2).

2.4 Oil Recovery – Protocol 2

The new procedure is shown in Fig. 5, it was performed without the phases related to glycerol-water solution. In this case only two oil recovery methods were used: water and polymer solution injection.

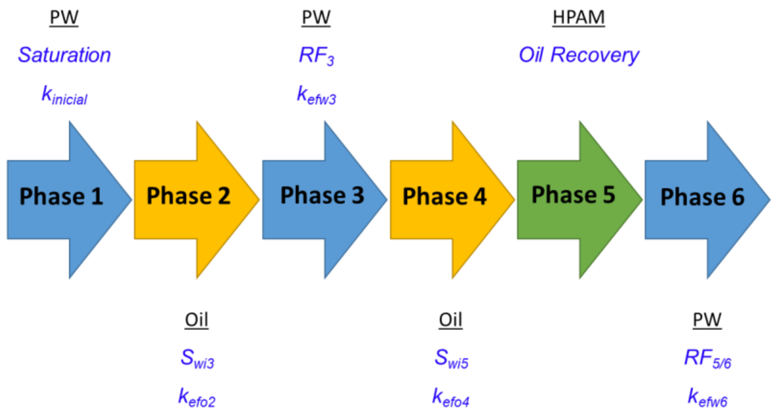

Figure 5. Schematics of oil recovery protocol 2.

3. RESULTS

Results of polymer adsorption tests showed a strong relationship between retention mechanisms, core permeability and mineralogical composition of porous medium walls. Core samples with low permeability presented high levels of retention that may be mainly caused by mechanical entrapment. Figures 6 and 7 illustrate the polymer ΔP coil and tracer (conductivity) breakthrough curves (left) and ΔP core (right) of GBT2 and BBT2, respectively. These figures show a graphical representation of a retention mechanism that is believed to be related to mechanical entrapment.

Sorbie (1991) described the phenomenon above, however there is no graphical representation of this in the literature. According to the author, this problem is very similar to deep-bed filtration. As polymer solution passes through the porous medium, the molecules would be trapped in the narrow pores. These would block, and flow in these elements would consequently reduce, probably trapping more molecules upstream of the blockage. During the filtration, the viscosity of solution that is flowing through the capillary tube is almost the same of the Peregrino-water, resulting in a slight increase of ΔP coil values. After blocking all the small pores, the solution would pass only through the wider capillaries, therefore ending the filtration process. At this time occurs the DP coil curve breakthrough.

In both cases, there is another clear indication that polymer chains could been trapped in porous medium since the ΔP across core test did not stabilize during slugs 1 and 2. Because of that, it was really difficult to quantify the real mass of polymer adsorbed on porous media walls by using the “two slug” method.

Results also revealed information related to the mineralogical composition of pore media walls for the low permeability core sample. As described in Tab. 1, BBT2 (Buff Berea) core permeability is greater than GBT2 (Gray Berea), however the latter presented a small value of polymer adsorption. It may be explained by the different mineralogical composition of the rocks, since the fraction of clay minerals is larger in Buff Berea core samples.

For the Bentheimer core, in which permeability is high and clay content is very low, results were good as shown in Fig. 8. Adsorption data are given in Tab. 4.

Table 4. Results from adsorption tests on sandstone core samples.

Core Sample	Permeability (mD)	Adsorption (μg/g)	RRF	IPV (%PV)
Gray Berea (GBT2)	58.46	82.98	2.48	13.32
Buff Berea (BBT2)	92.51	101.82	7.66	23.29
Bentheimer (BHT3)	1859	19.13	1.09	2.43

Oil recovery tests presented a similar tendency for low permeability rock types, as presented in Fig. 9 and Fig. 10. Polymer flooding seems to be the methodology that promotes higher oil recovery factors, followed by glycerol-water solution and brine (Peregrino-water). The benefits of polymer solution were revealed not only on the final recovery factor, but also on the oil production anticipation, as revealed on Fig. 11, for Bentheimer core samples. Table 5 shows the oil recovery data from protocol 1 and protocol 2.

Table 5. Results from oil recovery tests of residual resistance factor (RRF), recovery factor due to Peregrino water injection (RF_{PW}), recovery factor due to glycerol-water solution (RF_{GLY}), and recovery factor due to polymer solution (RF_{POL}) of protocol 1 and protocol 2.

Protocol 1					
Core Sample	Permeability (mD)	RRF	RF_{PW} (%)	RF_{GLY} (%)	RF_{POL} (%)
Gray Berea (GBT3)	65.82	3.08	32.39	40.44	51.40
Buff Berea (BBT3)	111.46	3.09	28.40	34.37	44.86
Bentheimer (BHT2)	2389	1.07	51.72	54.28	58.00
Protocol 2					
Core Sample	Permeability (mD)	RRF	RF_{PW} (%)	RF_{GLY} (%)	RF_{POL} (%)
Gray Berea (GBTH3)	69.66	2.90	31.54	-	47.22
Buff Berea (BB2C)	86.89	2.30	29.38	-	40.96
Bentheimer (BHTH3)	2204	1.19	55.95	-	54.96

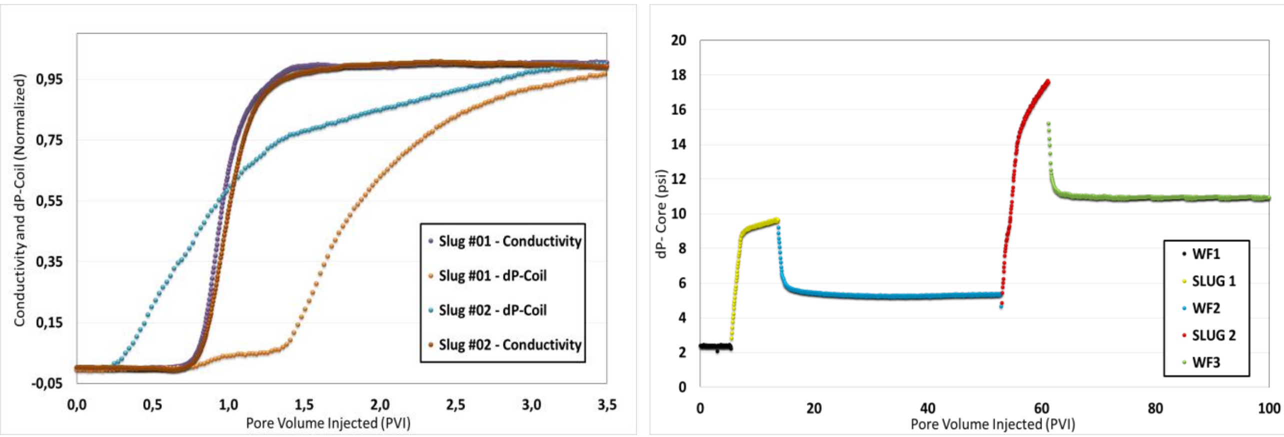

Figure 6. Polymer ΔP coil and tracer (conductivity) breakthrough curves of GBT2 (left) and ΔP core (right) as function of injected pore volume.

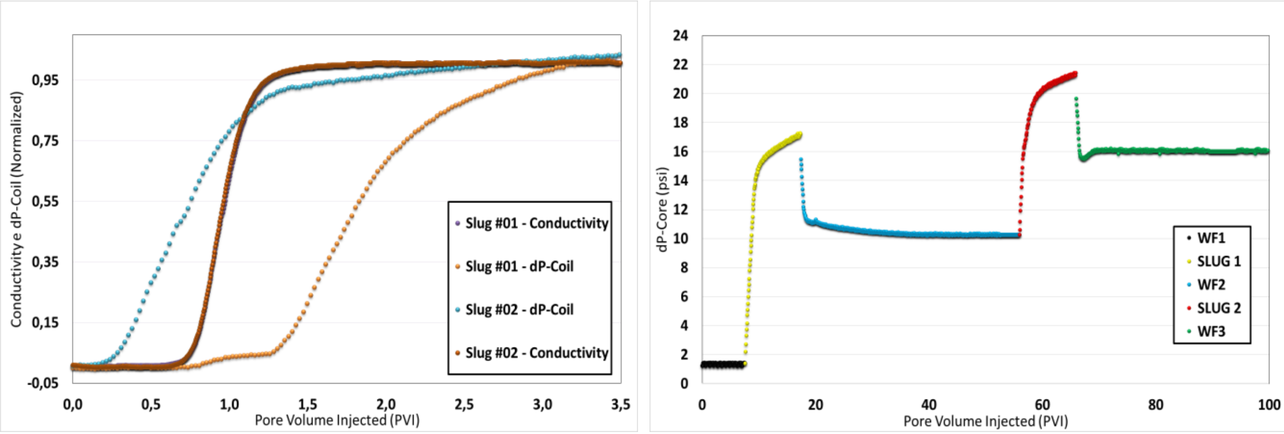

Figure 7. Polymer ΔP coil and tracer (conductivity) breakthrough curves of BBT2 (left) and ΔP core (right) as function of injected pore volume.

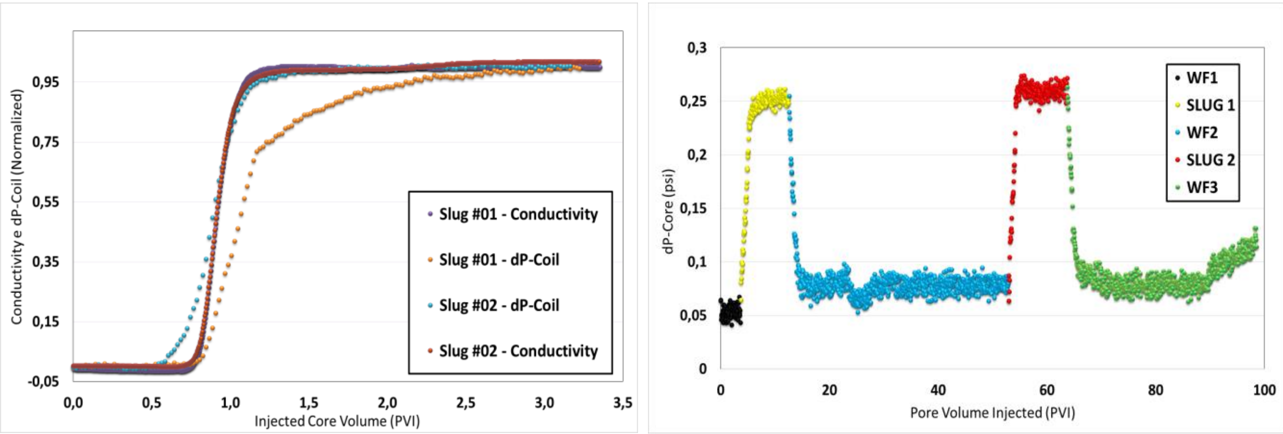

Figure 8. Polymer DP coil and tracer (conductivity) breakthrough curves of BHT3 (left) and ΔP core (right) as function of injected pore volume.

The graphs below are showing the results of oil recovery factor for protocols 1 and 2. Obtained values showed that the injection of glycerol-water solution has influenced the ORF of polymer solution for all tests. It should also be noted that, putting aside all effects that may be linked to the glycerol-water solution, all tests presented the same behavior *i. e.* the ORF using polymer solution showed better results, proving that the effects of polymer solutions into the reservoir during oil displacement go beyond the improvements in mobility ratio.

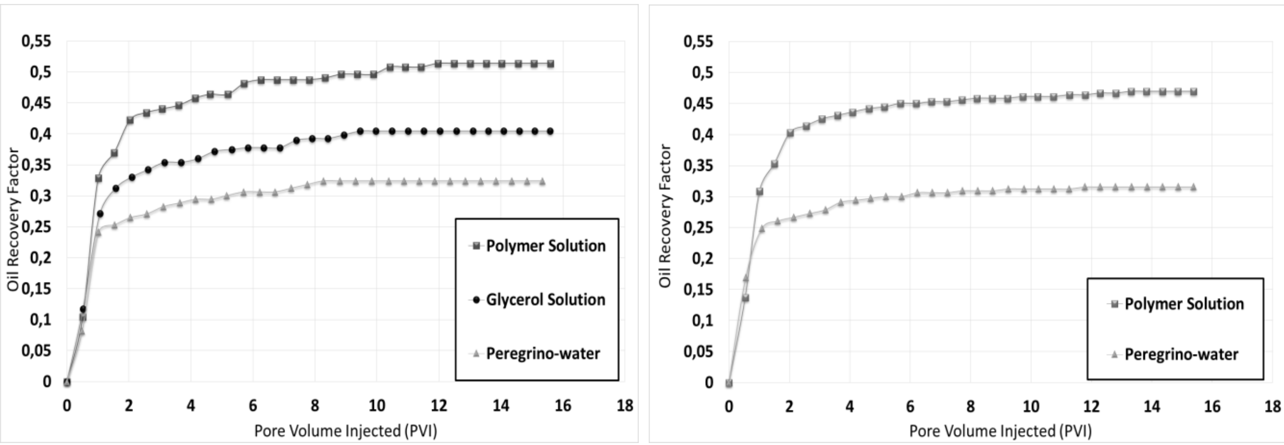

Figure 9. Results of oil recovery using protocol 1 (left) on GBT3 and protocol 2 (right) on GBTH3 as function of injected pore volume.

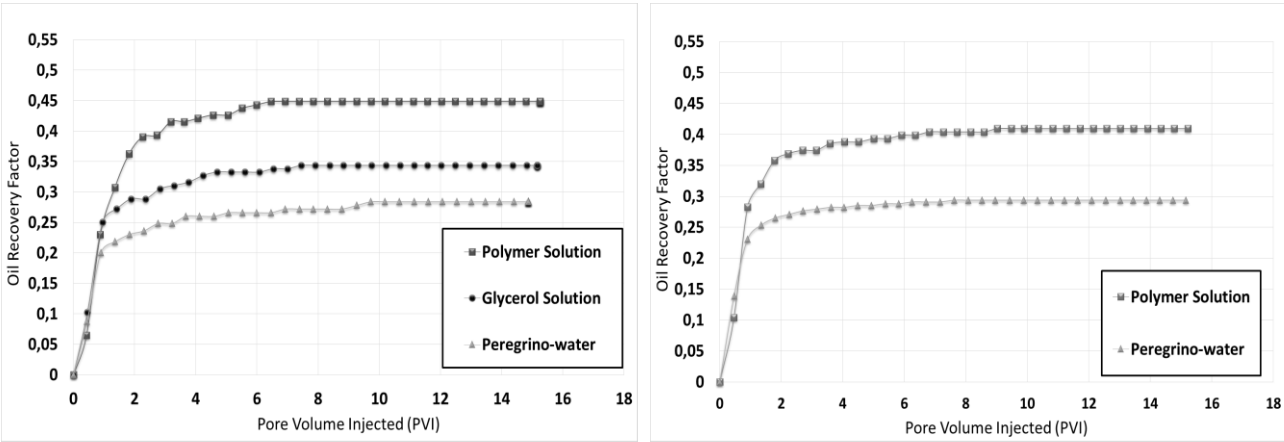

Figure 10. Results of oil recovery using protocol 1 (left) on BBT3 and protocol 2 (right) on BB2C as function of injected pore volume.

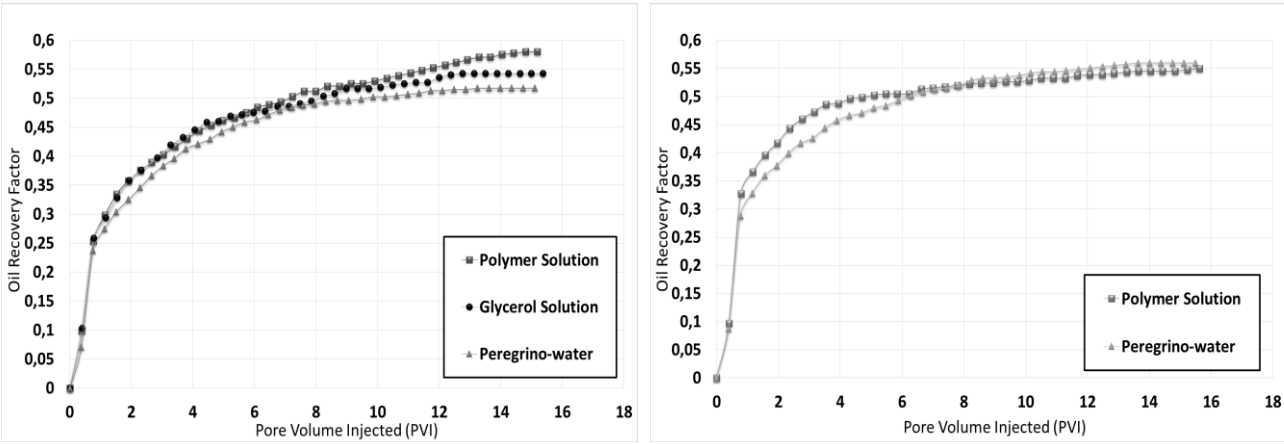

Figure 11. Results of oil recovery using protocol 1 (left) on BHT2 and protocol 2 (right) on BHTH3 as function of injected pore volume.

4. CONCLUSION

Polymer adsorption for three sandstone core samples were measured by recording the concentration profiles on the effluent from core flooding experiments. Results showed a clear relationship between polymer retention and petrophysical properties of test cores, such as permeability and mineralogical composition.

The improvements in oil displacement when compared to equivalent glycerol-water solution prove that besides the increase in viscosity of injection water that reduces the mobility ratio, polymer retention also plays a big role on oil recovery.

5. ACKNOWLEDGMENTS

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