





# Influence of physicochemical variables on polymer adsorption in porous media

Julia Herrera-Quintero<sup>*a*</sup>, Gustavo Maya-Toro<sup>*a*</sup>, Kelly Colmenares-Vargas<sup>*a*</sup>, Juliana Vidal-Prada<sup>*b*</sup>, Dalje Barbosa-Trillos<sup>*a*</sup> & Eduin Muñoz-Mazo<sup>*a*</sup>

<sup>a</sup> Ecopetrol S.A., Instituto Colombiano del Petróleo, Piedecuesta, Colombia, julia.herrera@ecopetrol.com.co, gustavo.maya@ecopetrol.com.co, dalje.barbosa@ecopetrol.com.co, kelly.colmenares@ecopetrol.com.co, eduin.munoz@ecopetrol.com.co <sup>b</sup> Universidad Industrial de Santander, Bucaramanga, Colombia; julianavidal33@hotmail.com

Received: July 22th, 2021. Received in revised form: October 6th, 2021. Accepted: October 22th, 2021.

## Abstract

HPAM type polymers and modifications with ATBS (Acrylamide Tertiary Butyl Sulfonated) units are used for EOR processes. Polymer adsorption is key to the success of these processes and is affected by variables such as molecular weight, hydrolysis, salinity, and permeability of the porous medium. Nevertheless, few studies corelate the dependence of these variables with adsorption. This work presents experimental results of the influence of variables on the dynamic adsorption of different polymers using sandstone type porous media. Modified polymers show adsorption less than 10  $\mu$ g/g in low permeability and Sor condition. The adsorption of modified HPAM and HPAM polymers has an inverse relationship with molecular weight and permeability. At higher molecular weight, fewer pores are accessed due to their hydrodynamic radius and lower permeability, greater mechanical and hydrodynamic retention. Water salinity and hardness are directly related to adsorption, with less influence for modified HPAM.

Keywords: HPAM; ATBS; adsorption; hydrolysis; permeability.

# Influencia de variables en la adsorción de polímero en medios porosos

## Resumen

Los polímeros tipo HPAM y modificaciones con unidades ATBS (Acrilamidas-Terbutil Sulfonadas) son usados para procesos EOR. La adsorción del polímero es clave en el éxito de estos procesos y es afectada por parámetros como el peso molecular, la hidrólisis, la salinidad y la permeabilidad del medio poroso. Sin embargo, pocos estudios relacionan la dependencia de estas variables con la adsorción. Este trabajo presenta resultados experimentales de la influencia de variables sobre la adsorción dinámica de diferentes polímeros empleando medios porosos tipo arenisca. Los polímeros modificados presentan adsorciones menores a 10 µg/g en baja permeabilidad. A mayor peso molecular, se acceden menos poros por su radio hidrodinámico y menor permeabilidad, mayor retención mecánica e hidrodinámica. La salinidad y dureza del agua tienen relación directa con la adsorción, con menos influencia para HPAM modificados.

Palabras clave: HPAM; ATBS; adsorción; hidrólisis; permeabilidad.

# 1. Introduction

Polymer flooding is one of the EOR techniques most employed at a commercial scale, with more than 865 projects reported worldwide [1,2]. The most successful projects have been developed in countries like China [3,4] and Canada [5-7], with incremental oil recoveries between 5 and 20%.

HPAM polymers, which are copolymers composed of AMD

(Amide) and AA (Acrylic Acid), are the most common substances used in EOR due to two main implications: the volumetric sweep efficiency improvement and the residual oil mobilization by viscoelastic effects [8-12]. However, the latter mechanism is questioned by some authors who suggest that reductions in the residual oil saturation are caused by wettability alteration [13]. HPAM polymers have limitations related to high temperature [14], high salinity, and hardness brine environments

How to cite: Herrera-Quintero, J., Maya-Toro, G., Colmenares-Vargas, K., Vidal-Prada, J., Barbosa-Trillos, D. and Muñoz-Mazo, E., Influence of physicochemical variables on polymer adsorption in porous media.. DYNA, 89(220), pp. 9-18, January - March, 2022.

[15,16]; contrary to modified AM-ATBS copolymers which present higher resistance to reservoir temperature and brine salinity [17]. It is worth considering that the success of a polymer flooding application, beyond the molecular structure of the polymer itself, relies on the understanding of additional concepts like retention [18], inaccessible pore volume [19], and permeability and mobility reduction [20].

Polymer retention has been identified as one of the most relevant variables in a polymer flooding process. It includes three complex mechanisms, which are difficult to calculate at porous media level: (1) Mechanical entrapment, (2) Hydrodynamic retention, and (3) Dynamic adsorption [21,22]. Adsorption is the most important mechanism. It occurs by chemical and physical interaction between the polymer backbone and the rock surface [23], such as Van der Waals forces, electrostatic interactions, and hydrogen bonds [21,22]. Nevertheless, besides adsorption on the rock surface, the polymer can be retained at pore structure by other phenomena like mechanical entrapment and hydrodynamic retention. At the laboratory level, it is hard to identify the dominant mechanism in polymer retention. Several scientific works have shown that dynamic adsorption is the main process responsible for retention in high permeability rock samples [24], while mechanical entrapment dominates dynamic adsorption in low permeability samples [24-27]. Nevertheless, few authors acknowledge the specific retention mechanism, and, in general, it is referred to as polymer's dynamic adsorption. This work will refer to polymer adsorption as a total retention mechanism.

In HPAM and modified HPAM copolymers, adsorption is considered an irreversible process [28-31] that likely to vary with injected polymer's concentration [32,33]. Furthermore, other variables affecting polymer adsorption like polymer type [16], MW [18,34], hydrolysis, polymer concentration, rock's mineral content, brine salinity and hardness [35,36], and rock permeability [20] have been studied given their importance to design efficient polymer flooding processes [34].

In sum, current literature refer to the dependence of HPAM polymer retention on variables like brine salinity, polymer hydrolysis, polymer concentration, and rock permeability. However, few studies consider AM-ATBS polymers to determine the correlation of these variables on polymer's adsorption. The purpose of this work was to perform experimental evaluations of HPAM and AM-ATBS copolymers to assess the effect of variables such as molecular weight, hydrolysis, brine salinity, brine hardness, and porous medium permeability on dynamic adsorption. This paper is aimed at improving understanding of this topic; and providing better guides to select the suitable polymer for a specific application, minimizing polymer losses and preventing possible blockage at pore scale.

# 2. Experimental development

# 2.1 Fluids

# 2.1.1 Brine

The synthetic brines were prepared by dissolving sodium chloride (NaCl), calcium chloride dihydrate (CaCl<sub>2</sub>\*2H<sub>2</sub>O),

Table 1.	
Brines	

Na <sup>+</sup> (mg/L) 0.2	K <sup>+</sup> (mg/L) 0.1	Ca <sup>++</sup> (mg/L)	Mg <sup>++</sup> (mg/L)	TDS (mg/L)	Cl <sup>-</sup> (mg/L)	R <sup>+</sup>
0.2			(mg/L)	(mg/L)	(mg/L)	
	0.1				(mg/L)	(%)
	0.1	0	0	100	6	0
5239	29.2	270	37.2	14000	9021	2.9
400	16.8	29.8	6.5	1400	140	4.1
306	17.0	30	3	1000	279	5.3
2733	59.9	276	61.6	9000	4809	5.5
630	50.7	77.9	14.6	2000	949	6.6
64.1	1.2	12.8	0.8	300	32	10.2
140	12.1	32.0	3.0	596	217	11.6
	2733 630	273359.963050.764.11.2	273359.927663050.777.964.11.212.8	273359.927661.663050.777.914.664.11.212.80.8	273359.927661.6900063050.777.914.6200064.11.212.80.8300	273359.927661.69000480963050.777.914.6200094964.11.212.80.830032

Source: The Authors

Table 2. Polymer molecules.

Sample ID	Polymer type	Composition	Hydrolysis (%)	Molecular Weight (10 <sup>6</sup> MDa)	
1		AMD/AA	30.0	5.0	
2		AMD/AA	25.0	6.0	
3	IIDAM	AMD/AA	30.0	9.0	
4	HPAM	AMD/AA	28.0	9.0	
5		AMD/AA	30.0	10.0	
6		AMD/AA	30.0	20.0	
7		AMD/AA/ATBS	25.0	6.0	
8		AMD/AA/ATBS	12.0	8.0	
9	HPAM MODIFIED	AMD/AA/ATBS	25.0	8.0	
10		AMD/ATBS	25.0	8.0	
11		AMD/ATBS	32.0	8.0	
12		AMD/ATBS	25.0	13.0	
13		AMD/AA/ATBS	20.0	25.0	

Source: The Authors

potassium chloride (KCl), and magnesium chloride hexahydrate (MgCl<sub>2</sub>\*6H<sub>2</sub>O) in de-ionized water. Brines were filtered through a 0.45-micron cellulose-like membrane. The properties used to differentiate the brines were the amount of total dissolved solids (TDS, in mg/L) and hardness ( $R^+$ ), defined as the molar ratio of divalent cations and the total number of moles of cations in the brine (eq 1):

$$R^{+} = \frac{[Cdiv]}{[Cmono] + [Cdiv]} \tag{1}$$

where;

[Cdiv]: number of moles of divalent cations in the brine. [Cmono]: number of moles of monovalent cations in the brine. Table 1 lists the brines used in this research, where

hardness values range from 0 to 11.6%.

# 2.1.2 Polymers

Powder partially hydrolyzed polyacrylamides (HPAM) and HPAM polymers modified with Acrylamide-Terbutyl-Sulfonated units (ATBS) were used. Table 2 shows the polymer molecules used and some chemical characteristics.

# 2.2 Polymeric solution preparation

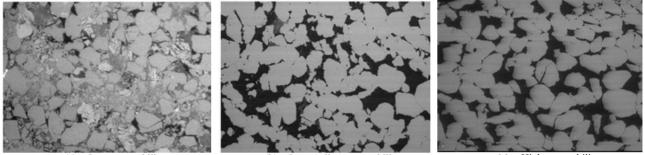
Stock polymer solutions of 5,000 ppm were prepared according to API RP63 (American Petroleum Institute, 1990) [37]. The polymer powder was slowly added to the vortex

Scenarios	Permeability (mD)	Porosity (%)	<b>Total Rock Composition</b>		Less than 2 µm fraction composition			
			Quartz	Clays	Illite	Smectite	Kaolinite	Others
			(%)	(%)	(%)	(%)	(%)	(%)
Low	30 - 500	10-20	90	10	24	29	42	5
Intermediate	500 - 1000	15-25	90	5	18	ND*	62	20
High	>1000	15-25	88	5	<6	ND*	66	18

Table 3. Porous media characteristics

ND\*: Not Detected.

Source: The Authors



(a) Low permeability

(b) Intermediate permeability

(c) High permeability

Source: The Authors

Figure 1. Morphology and composition of the porous media used.

formed by the preparation waters (Table 1) under stirring mechanical conditions. Stirring is maintained until complete dissolution of the polymer is achieved. The final solution used is obtained from diluting the stock solution with the preparation water at concentrations defined in Table 4.

# 2.3 Viscosity measurement

Polymer solution viscosities were measured at 30°C and at 7.3 s-1 using the Brookfield LVT viscosimeter with ULA 0 or Din 86 adapter. Each measurement was performed 4 times and the mean value of the measurements was calculated and reported on the graphs.

#### 2.4 Porous reservoir media

Table 3 shows the petrophysical characteristics of the porous media. They are classified as low, medium, and high permeability porous media. The dimensions of the samples were 1.5 inches in diameter and 2.36 inches in length approximately. The porous media used correspond to rock samples from consolidated sandstone-type deposits characterized mainly with quartz mineralogy (90%) with variable clay mineral ratios. The high and intermediate permeability samples have lower clay content (5%), with Kaolinite being the mineral with the highest and Illite with the lowest proportions. In contrast, low permeability samples have a higher clay content (10%), and there is a large amount of Smectite-type mineral in addition to Kaolinite and Illite. Fig. 1, photographs of the pore space of the media used with low, medium, and high permeability.

Thirteen experimental evaluations were carried out with clean porous media and a single fluid in the saturation phase (100% brine, Sw 100%). Other assessments were carried out

with porous media with restored wettability at residual oil saturation (Sor).

# 2.5 Adsorption experiments in displacement equipment

The experiments were performed in core flooding devices using an ISCO-type injection pump at a constant flow rate. The equipment has a core holder and four differential pressure sensors of different ranges to determine the pressure drop through the porous medium (Fig. 2). The core holder has a heating jacket to bring the porous media and injection fluids to the desired temperature. The temperature for the experiments was set from 50°C to 100°C.

Twenty-five displacement tests were carried out to obtain information on dynamic adsorption of HPAM and modified HPAM polymer solutions in porous media under the experimental conditions described in Table 4. In the first thirteen experiments, adsorption in porous media without restoration of wettability and a single fluid as the saturating phase (100% water).

The other twelve experiments evaluate adsorption on porous media with restored wettability. For restored wettability, the porous medium was first saturated with brine (solvent of the polymer solution to be injected in the medium). Next, the permeability brine was measured at two different injection rates. Then, crude oil was injected and the permeability at crude oil was measured and the porous medium was aged at reservoir temperature for sufficient time to establish adsorption equilibrium. Finally, the brine was injected until reaching residual oil saturation condition.

The adsorption evaluation was carried out by injecting the polymeric solution together with a tracer in the porous medium until the concentrations of polymer and tracer produced were equal to the injected concentrations. Then, the brine injection was carried out until the non-production of polymer and tracer in the effluent was evident. Finally, the second batch of polymer and tracer solution was injected until the exit concentrations were equal to those at the inlet.

#### 2.6 Determination of adsorption

The method used to calculate polymer adsorption was the concentration profile method, which requires breakthrough curves. This method indicates that adsorption and IPV can be calculated directly with the values corresponding to the normalized concentration point (Ce / Cinj) at 0.5 [24,38,39]. Adsorption is estimated as the difference between the 0.5 normalized concentration value of the first and second polymer slug (eq. 2).

$$Adsorption = VP_{1-slug\frac{Ce}{Cinj}=0.5} - VP_{2-slug\frac{Ce}{Cinj}=0.5}$$
(2)

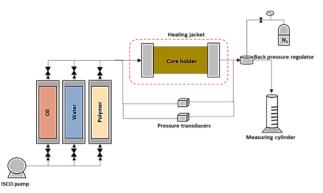


Figure 2. Experimental setup for polymer adsorption evaluation in porous media. Source: The Authors

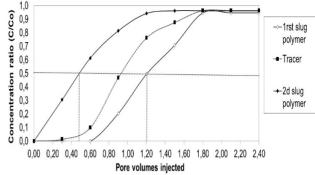


Figure 3. Example polymers adsorption in porous media saturated with brine to Sw 100%, test 2. (See details of the experiments in Table 4). Source: The Authors

# 3. Results and discussion

#### 3.1 Polymer adsorption

# 3.1.1 Polymer adsorption test 2 (300 ppm - HPAM polymer)

Fig. 3 shows a typical example of the raw experimental data used to estimate the reported adsorption for the second experiment. The results show that the first polymer slug is delayed and exits at 1.2 VP and the second slug is ahead and exits at 0.45 VP. HPAM adsorption was calculated with eq. (2), obtaining a value of 255.4 lb/acre-ft (41.2  $\mu$ g / g of rock) was obtained. This procedure was realized for the twenty-five displacement tests carried out in the different porous media.

Test Polymer type		Samula ID	Fluid content	Brine	Polymer	Test	Viscosity	Permeability
Test	Polymer type	Sample ID	Fiuld content	Drine	concentration (ppm)	temperature (°C)	@ test temperatura (cP)	(mD)
1		1		S1	300	50	8.6	184
2		5		S1	300	50	9.9	147
3		3		S2	500	60	5.4	95
4	HPAM	6	Sw 100%	S3	1000	60	45.1	3710
5		1		S5	1000	60	4.3	38
6		2		S5	1000	60	3.7	21
7		4		S5	1000	60	5.4	47
8		9		S4	750	100	18.0	758
9		11		S6	1500	100	24.7	3565
10	MODIFIED	7	Sw 100%	S7	300	50	11.4	140
11	HPAM	9	SW 100%	<b>S</b> 8	1000	90	40.0	2555
12		12		<b>S</b> 8	1000	90	35.8	2978
13		13		<b>S</b> 8	750	90	37.6	2569
14		1		S1	300	50	8.6	420
15	HPAM	5	Sor	S1	300	50	9.9	147
16		3		S2	500	60	5.4	119
17		1		S5	1000	60	4.3	38
18		7		S7	300	50	11.4	79
19		8		S2	500	60	3.7	93
20		9		S4	750	100	18.0	696
21	MODIFIED	10	Sor	S6	1500	100	22.6	3364
22	HPAM	12		S6	1000	100	35.8	3063
23		9		<b>S</b> 8	1000	90	40.0	4693
24		12		<b>S</b> 8	1000	90	35.8	4302
25		13		S8	750	100	37.6	3179

Table 4.Summary of adsorption studies in porous media

Source: The Authors

# 3.2 Effects of the type of polymer

Fig. 4 shows the adsorption results obtained for HPAM and HPAM polymers modified with sulfonated groups (ATBS) in porous media, 100% saturated with brine; Fig. 5 shows the results in porous media under residual oil saturation conditions. Results demonstrate that polymers HPAM present the highest adsorption in either saturation conditions evaluated (Sw 100% and Sor), reaching values of 1288 lb/acre-ft (224 µg/g of rock) when the superficial area of the porous media is fully exposed to the polymer (Sw 100%). This adsorption is reduced to values close to 600 lb/acre-ft (100 µg/g of rock) when the porous media carried out a wettability restoration process and is assessed under the condition of residual oil trapped in the pores. Otherwise, modified HPAM polymers show lower adsorption values (<100 lb/acre-ft or 17.5 µg/g of rock) under the most critical condition (Sw 100%). Its adsorption is further reduced in Sor scenarios with values lower than 40 lb/acre-ft (7 µg/g of rock).

It is worth to highlight that the porous media used for evaluating HPAM polymers at Sw 100% and Sor are very high as compared to modified HPAM, particularly in experiment #3. This is because these experiments used low and intermediate permeability porous media, where the possible mineralogy (Illite and Smectite) and pore structure are a relevant components in the mechanical entrapment phenomenon. Moreover, the results conclude that wettability in porous media affects the polymer adsorption, and possibly the adsorption values reported in porous media without oil are not representative.

On the other hand, the experimental results show that the dynamic adsorption of HPAM polymers under Sw 100% conditions is twice the adsorption in Sor condition; this same trend was observed for modified HPAM.

Our results in the reservoir rock coincide with Szabo (1975). This study reported that modified polymers with ATBS showed lower adsorption than HPAM using Berea core samples with similar properties. The experimental data presented adsorption values ranging from 35 lb/acre-ft (6.  $\mu$ g/g of rock) to 72 lb/acre-ft (12  $\mu$ g/g of rock) for modified HPAM polymer and between 88 lb/acre-ft (15  $\mu$ g/g of rock) and 196 lb/acre-ft (34  $\mu$ g/g of rock) [25].

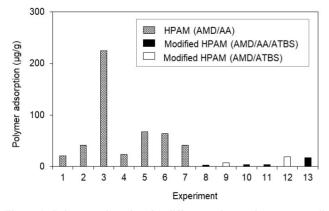


Figure 4. Polymers adsorption for different polymers in porous media saturated with brine to Sw 100% (See details of the experiments in Table 4). Source: The Authors

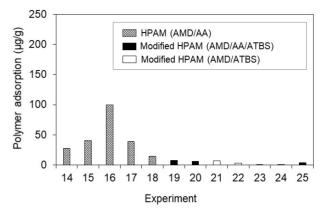


Figure 5. Polymers adsorption for different polymers in porous media with residual oil saturation (Sor). See details of the experiments in Table 4. Source: The Authors

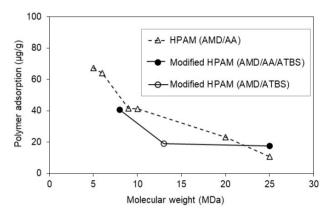


Figure 6. Polymer adsorption according to the molecular weight in porous media saturated with brine to Sw 100%. Source: The Authors

# 3.3 Effects of the molecular weight in the polymer adsorption

Experimental evaluation results suggest that the adsorption hydrolyzed polyacrylamide (HPAM) decreases with the molecular weight increasing in both saturation conditions evaluated at Sw 100% (Fig. 6) and Sor (Fig. 7). Results are coherent, considering that the higher MW does not access the smallest porous because of the hydrodynamics radio and, therefore, there was less adsorption.

Experimentally, HPAM adsorption values evidence decreases up to 10 times with five times the increase in the molecular weight of the polymer under the condition of Sw 100% (Fig. 6). Otherwise, at Sor condition, for MW higher than 9 MDa, there is no representative change in the adsorption value (Fig. 7). These results suggest that a critical point of molecular weight exists above which the adsorption stabilizes when no mobile oil is present in the porous media. It is possible that in the smallest pores of the reservoir rock at Sor conditions, the oil is trapped due to capillary effects. There is no evidence of adsorption change in the largest pores with the increase of polymer molecular weights.

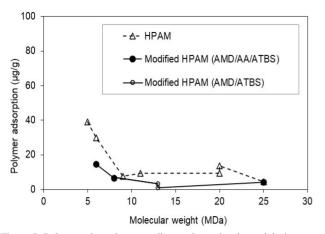


Figure 7. Polymer adsorption according to the molecular weight in porous media with residual oil saturation (Sor). Source: The Authors

Literature reports the highest levels of dynamic adsorption as the MW of polymers increase [40-42]; this is consistent with the theory that a high molecular weight polymer could form a thicker polymer layer when the polymer is adsorbed on the surface [43].

The modified HPAM with sulfonated groups present adsorption reductions with the increase of polymer MW in both saturation conditions (Sw and Sor). However, it is less pronounced compared to the HPAM polymers. It is observed that the sulfonated group reduces adsorption values and molecular weights greater than 13 MDa. There are no significant changes in the adsorption, which could mean that it stabilizes after this molecular weight.

# 3.4 Effect of the polymer hydrolysis

The literature has shown that HPAM adsorption presents an inverse relation with the hydrolysis percentage, concluding that the hydrolysis degree and the solution electrolytes concentration influence more in the adsorption than the molecular weight [44]. These research experimentation results are consistent with previous results; while the HPAM polymer hydrolysis degree increase, the adsorption on the porous media in either saturation evaluated decreases (Sw 100% and Sor), where the adsorption is so much lower when residual oil is present in the porous media. This result is because a higher hydrolysis degree gives rise to greater electrostatic repulsion between the carboxyl group charge of the polymer (negative charge) and the rock surface (negative charge) and consequently decreases adsorption.

However, there is a minimum adsorption value that does not depend on the hydrolysis degree. This minimal adsorption depends on other interactions (Van der Waals and electrostatic forces, and hydrogen bonds).

The modified HPAM polymer with ATBS units is observed with the same trend of adsorption decrease according to the hydrolysis grade; however, it should be noted that modified HPAM polymers present lower adsorption than HPAM polymers in both scenarios assessed (Fig. 8 and Fig. 9). Possibly, the sulfonation grade of modified HPAM polymer increases the negatives charges in the polymer structure and, therefore, the adsorption decreased in the porous media. Szabo (1979) found a similar trend and concluded that the HPAM polymers are adsorbed more than the modified HPAM polymers [27].

#### 3.5 Salinity effect on the adsorption

The increase of water salinity used for preparing the polymer increase the adsorption level. Salinity is one of the significant factors that directly affect the polymer's chemical, mechanical and thermal stability [14,16,45]. The type of charge (positive, negative, or neutral) of the rock surface changes with the salinity, causing a different behavior on the rock surface. A low concentration of  $Ca^{+2}$  ions promotes the adsorption of HPAM polymer on silica due to divalent ions compressing the flexibles HPAM molecules' size and reducing the static repulsion between the silica surface and the polymer's carboxyl groups [46]. Additionally, Smith's results showed that the dynamic adsorption of polymer could be six times higher with a change in the water salinity used for preparing the polymer solution from 1% to 10% NaCl.

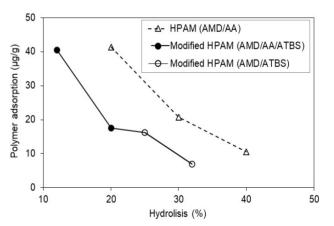


Figure 8. Polymer adsorption as a function of the polymer hydrolysis degree in porous media saturated with brine to Sw 100%. Source: The Authors

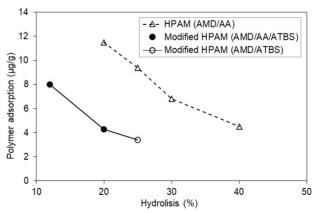


Figure 9. Polymer adsorption as a function of the polymer hydrolysis degree in porous media with residual oil saturation (Sor). Source: The Authors

The modified polymers with a high sulfonation degree decrease the adsorption in with high salinity and content of divalent ions scenarios[44]. However, the efficiency of these polymers depends mainly on their manufacturing process. Similarly, a polymer manufactured through a post-hydrolysis process is more sensitive to divalent ions content than a polymer obtained through copolymerization.

This research shows that HPAM polymer and modified HPAM polymer adsorption is directly related to the polymer's preparation water salinity for both conditions, Sw 100% (Fig. 10) and Sor (Fig. 11) being lower for the state of residual oil saturation. The adsorption values are reduced up to 5.5 times when used modified HPAM polymer with sulfonated groups in the more critical scenario (Sw 100%) and approximately 18 times in the residual oil saturation scenario at the highest salinity condition of 14000 ppm. In terms of salinity, trends of modified polymers corroborate that polymers with sulfonated groups (ATBS) are resistant in adverse high salinity conditions in some reservoirs, and possibly, these molecules aid the polymer flooding processes in high salinity reservoirs.

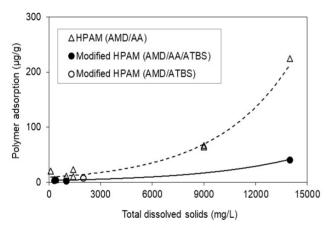


Figure 10. Polymer adsorption as a function of the salinity in porous media saturated with brine to Sw 100%. Source: The Authors

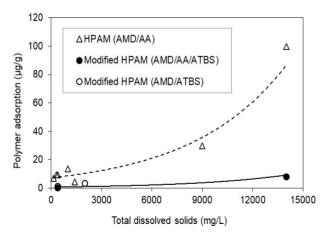


Figure 11. Polymer adsorption as a function of the salinity in the porous media with residual oil saturation (Sor). Source: The Authors

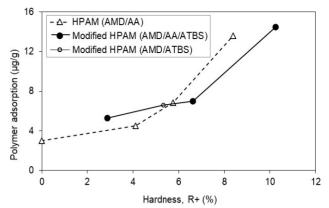


Figure 12. Polymer adsorption as a function of the hardness  $(R^+)$  in the porous media at residual oil saturation (Sor) conditions. Source: The Authors

With respect to water hardness, just as for the salinity, it is evidenced that the adsorption increases when increasing the polymer's preparation water hardness (Fig. 12). HPAM polymers with hardness values below 6% have lower adsorption than the modified polymers with sulfonated groups, possibly caused by the modified polymers' manufacturing process. In spite of their chemical and thermal resistance, they continue having operation limits for reservoirs with high salinity, hardness, and temperature. Additionally, the adsorption results below 6% of hardness show quite low adsorption values for both molecule type assessed. It may be concluded that, below this hardness value, the adsorption in sandstones is less than 7  $\mu$ g/g of rock.

# 3.6 Permeability effect

Polymer retention and adsorption are reduced according to permeability increase due to the decrease of phenomena such as the polymer mechanic entrapment on the smaller pore throat. Another variable that has a significant influence on polymer retention is the clay content. Therefore, rock samples with low permeability and high content clay raise the retention values.

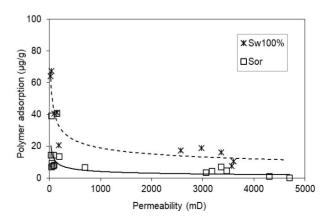


Figure 13. Polymer adsorption in terms of permeability in porous media at Sw 100% y Sor. Source: The Authors

In this research work, the rock samples are sandstone with Kaolinite as the major clay mineral. The results are consistent with those reported in the literature (for both scenarios assessed), whereas there is higher permeability and, lower polymer adsorption. In the case of Sw 100% (Fig. 13), higher adsorption values were obtained due to higher surface contact of the polymer solution with the porous media.

# 4. Conclusions

This research compared the results of dynamic adsorption of HPAM polymers and modified HPAM polymers according to molecular weight, hydrolysis degree, salinity, water hardness, and permeability in two different saturation scenarios: Sw 100% and Sor. Based on the analysis of the results, it may be concluded that:

- 1. The chemical structure of the polymers has a significant influence on the dynamic adsorption; polymers with modified structure (ATBS) show adsorption values below than  $10 \ \mu g/g$  at low permeability and Sor conditions.
- 2. It is a common practice in the industry to perform adsorption tests with 100 % water saturation. However, the results show that this is not a representative condition for oil reservoirs. Polymer adsorptions strongly depend on the saturation condition of porous media.
- 3. The HPAM and the modified HPAM polymer's molecular weight presents an inverse relationship with the dynamic adsorption. The polymers with higher MW should face constrained access in the porous media.
- 4. When the hydrolysis degree of the HPAM polymers increases, the adsorption goes down; the adsorption is also low when the porous media have a residual oil saturation. This behavior can be explained because higher polymer hydrolysis can generate a more significant electrostatic repulsion between the carboxyl group's charge (negative charge) and the rock surface (negative charge). However, there is a minimum adsorption value that doesn't depend on the hydrolysis degree.
- 5. Modified HPAM polymers with ATBS units show the same tendency that HPAM polymers, although with lower adsorption values. The sulfonation degree of modified HPAM increases negative charges in the polymer structure, decreasing the adsorption on the porous media.
- 6. The salinity and hardness of water show a direct relationship with adsorption for the two types of molecules (HPAM and modified HPAM), but modified HPAM's are more resistant to high salinity and hardness conditions. Modified HPAM evidence 50% less adsorption at the same conditions compared with HPAM.
- 7. The increase of the porous medias's permeability reduces the HPAM and modified HPAM adsorption.
- 8. The dynamic adsorption of HPAM polymers under Sw 100% conditions is twice the adsorption under Sor condition; modified HPAM show the same behavior.

#### Acknowledgments

The authors wish to thank Centro de Innovación y Tecnología ICP for authorization to publish these results.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

# References

- Saleh, L., Mingzhen, W., Yandong, Z. and Baojun, B., Data analysis and novel screening criteria for polymer flooding base on a comprehensive database. SPE-169093-PA. SPE Reservoir Evaluation & Engineering Preprint, pp. 1-18, 2016. DOI: 10.2113/169093-PA.
- [2] Manrique, E., Ahmadi, M. and Samani, S., Historical and recent observations in Polymer Floods: an update review. CT&F - Ciencia, Tecnología y Futuro, 6(5), pp. 17-48. 2017. DOI: 10.29047/01225383.72.
- [3] Zhang, Y., Wei, M., Bai, B., Yang, H. and Kang, W., Survey and data analysis of the pilot and field polymer flooding projects in China. SPE Improved Oil Recovery Symposium, Tulsa, OK. SPE-179616. 2016. DOI: 10.2118/179616-MS.
- [4] Sheng, J., Bernd-Leonhardt, J. and Nasser, A., Status of polymer flooding technology. Journal of Canadian Petroleum Technology, 54(02), pp. 116-26, 2016. DOI: 10.2118/174541-PA.
- [5] Renouf, G., A survey of polymer flooding in western Canada. SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma. SPE-169062. 2014. DOI: 10.2118/169062-MS.
- [6] Delamaide, E., Tabary, R., Rénard, G. and Dwyer, P., Field scale polymer flooding of heavy oil: the Pelican Lake story. 21<sup>st</sup> World Petroleum Congress, Moscow, Russia. WPC 21-0851, 2014b.
- [7] Delamaide, E., Zaitoun, A., Renard, G. and Tabary, R., Pelican Lake field: first successful application of polymer flooding in a heavy-oil reservoir. SPE Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia. SPE165234. 2013. DOI: 10.2118/165234-MS.
- [8] Deming, W., Wang, G., Wu, W., Xia, H. and Yin, H., The influence of viscoelasticity on displacement efficiency-from micro- to macroscale. SPE-109016-MS. SPE Annual Technical Conference, pp. 1-10, 2007. DOI: 10.2118/109016-MS.
- [9] Deming, W., Xia, H., Yang, S. and Wang, G., The influence of viscoelasticity on micro forces and displacement efficiency in pores, cores and the field. SPE-109016-MS. SPE EOR Conference at Oil & Gas West Asia, pp. 1-18, 2010. DOI: 10.2118/109016-MS.
- [10] Deming, W., Wang G. and Xia, H., Large scale high viscous-elastic fluid flooding in the field achieves high recoveries. SPE-144294-MS. SPE Enhanced Oil Recovery Conference, 1921 July, Kuala Lumpur, Malaysia, pp. 1-7, 2011. DOI: 10.2118/144294-MS.
- [11] Clarke, A., Howe, A.M., Mitchell, J., Staniland, J. and Hawkes L.A., How viscoelastic-polymer flooding enhances displacement efficiency. SPE-174654-PA. SPE Journal, 21(03), pp. 675-687, 2016. DOI: 10.2118/174654-PA.
- [12] Koh, H., Vicent, B.L. and Gary, A., Pope. Experimental Investigation of the effect of polymers on residual oil. SPE-179683-PA. SPE Journal, Preprint, 2016. DOI: 10.2118/179683-PA.
- [13] Seright, R.S., How much polymer should be injected during a polymer flood?. Review of previous and current practices. In: IOR 2017-19<sup>th</sup> European Symposium on Improved Oil Recovery, 2017. DOI: 10.2118/179543-MS.
- [14] Gaillard, N., Giovannetti, B., Leblanc, T., Thomas, A., Braun, O. and Favero, C., Selection of Customized polymers to enhance oil recovery of high temperature reservoirs. In: SPE Latin American and Caribbean Petroleum Engineering Conference, Quito, 2015. SPE 177073-MS, 2015. DOI: 10.2118/177073-MS.
- [15] Gaillard, N., Giovannetti, B. and Favero, C., Improved oil recovery using thermally and chemically protected compositions based on Coand Ter-Polymers containing acrylamide. In: SPE Improved Oil Recovery Symposium, Tulsa, 2010. SPE 129756-MS. DOI: 10.2118/129756-MS.
- [16] Gaillard, N., Giovannetti, B., Favero, C., Caritey, J.P., Dupuis, G. and Zaitoun, A., New water soluble NVP acrylamide terpolymers for use in EOR in Harsh conditions. In: SPE Improves Oil Recovery Symposium, Tulsa, 2014. SPE 169108-MS. DOI: 10.2118/169108-MS.
- [17] Vermolen, E.C., Van Haasterecht, M.J., Masalmeh, S.K., Faber, M.J. and Boersma, D.M. and Gruenenfelder, M., Pushing the envelope for polymers. presented at the SPE middle-east oil and gas show and

conference, Manama, 2011. SPE 141497-MS. 2011. DOI: 10.2118/141497-MS.

- [18] Al-Hashmi, A.R., Luckham, P.F., Heng, J.Y.Y., Al\_Maamari, R.S., Zaitoun, A., Al-Sharji, H.H. and Al-Wehaibi, T.K., Adsorption of high-molecular wight EOR polymers on glass surfaces using AFM and QCM. Energy & Fuels, 27, pp. 2437-2444, 2013. DOI: 10.1021/ef302143a.
- [19] Dawson, R. and Lantz, R.B., Inaccessible pore volume in polymer flooding. Society Petroleum Engineer Journal, SPE-3522-PA, 12(5), pp. 448-452, 1972. DOI: 10.2118/3522-PA.
- [20] Guetni, I., Marliére, C., Roussear, D., Pelletier, M., Bihannic, I. and Villiéras, F., Transport of EOR polymer solutions in low permeability porous media: impact of clay type and injection water composition. Journal of Petroleum Science and Engineering, 186, art. 106690, 2019. DOI: 10.1016/j.petrol.2019.106690.
- [21] Sorbie, K.S., Polymer-improved oil recovery. Springer Science & Business Media, Berlin/Heidelberg, Germany. 2013.
- [22] Sheng, J., Modern chemical enhanced oil recovery: Theory and practice, 1<sup>st</sup> ed., Gulf Professional Publishing, Houston, TX, USA. 2010.
- [23] Theng, B.K.G., Chapter 2: Polymer behavior at clay and solid surfaces. In: Developments in soil science, formation and properties of clay- polymer complexes. Elsevier Science B.V., Amsterdam, The Netherlands, 1979.
- [24] Huh, C., Lange, E.A. and Cannella, W.J., Polymer retention in porous media. In: Proceedings of the SPE/DOE Enhanced Oil Recovery Symposium, SPE-20235-MS, Tulsa, OK, USA, 1990. DOI: 10.2118/20235-MS.
- [25] Szabo, M.T., Some aspects of polymer retention in porous media using a C14-tagged hydrolyzed polyacrylamide. Soc. Pet. Eng. Journal 15(04), pp. 323-337, 1975. SPE-4668-PA, DOI: 10.2118/4668-PA.
- [26] Dominguez, J.G. and Willhite, G.P., Retention and flow characteristics of polymer solutions in porous media. Soc. Pet. Eng. J. SPE-5835-PA, 17(02), pp. 111-121, 1977. DOI: 10.2118/5835-PA.
- [27] Szabo, M.T., An evaluation of water-soluble polymers for secondary oil recovery—Parts 1 and 2. Journal of Pet. Technol., 31(05), pp. 553-570, 1979. SPE-6601-PA. DOI: 10.2118/6601-PA.
- [28] Lecourtier, J. and Chauveteau, G., Propagation of polymer slugs through porous media. In: SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers. SPE-13034-MS, 1984. DOI: 10.2118/13034-MS.
- [29] Chauveteau, G. and Kohler, N., Polymer flooding: the essential elements for laboratory evaluation. In: SPE Improved Oil Recovery Symposium. Society of Petroleum Engineers. SPE-4745-MS. 1974. DOI: 10.2118/4745-MS.
- [30] Bagassi, M., Chauveteau, G., Lecourtier, J., Englert, J. and Tirrell, M., 1989. Behavior of adsorbed polymer layers in shear and elongational flows. Macromolecules 22(1), pp. 262-266, DOI: 10.1021/ma00191a049.
- [31] Pefferkorn, E., Polyacrylamide at Solid/Liquid interface. J. Colloid Interface Sci. 216(2), pp. 197-220, 1999. DOI: 10.1006/jcis.1999.6312.
- [32] Zhang, G. and Seright, R., Effect of concentration on HPAM retention in porous media. SPE-166265-PA SPE J. 19(03), pp. 373-380, 2014. DOI: 10.2118/166265-PA.
- [33] Rodriguez, F., Rousseau, D., Bekri, S., Djabourov, M. and Bejarano, C., Polymer flooding for extra-heavy oil: new insights on the key polymer transport properties in porous media. SPE International Heavy Oil Conference and Exhibition, SPE 172850, 2014. DOI: 10.2118/172850-MS.
- [34] Guo, H., How to select polymer molecular weight and concentration to avoid blocking in polymer flooding. SPE Symposium: Production Enhancement and Cost Optimization, Malaysia, 2017. SPE-189255-MS, 2017. DOI: 10.2118/189255-MS.
- [35] Divers, T., Gaillard, N., Bataille, S., Thomas, A. and Favéro C., Successful polymer selection for CEOR: brine hardness and mechanical degradation considerations. Society of Petroleum Engineers, SPE Oil and Gas India Conference, Mumbai, India, 2017. SPE-185418-MS, 2017. DOI: 10.2118/185418-MS.
- [36] Thomas, A., Gaillard, N. and Favero, C., Some key features to consider when studying acrylamide-based polymer for chemicals

enhanced oil recovery. Oil & Gas Science and Technology, 67(6), pp. 887-902, 2013. DOI: 10.2516/ogst/2012065.

- [37] RP63, A. P. I., Recommended practices for evaluation of polymers used in enhanced oil recovery operations. Washington, USA, 1990.
- [38] Li, K., Jing, X., He, S. and Wei, B., Static adsorption and retention of viscoelastic surfactant in porous media: EOR implication. Energy Fuels, 30(11), pp. 9089-9096. 2016. DOI: 10.1021/acs.energyfuels.6b01732.
- [39] Wang, J., Lu, H. and Luo, P., Determination of inaccessible pore volume and retention pore volume by the use of effluent concentration profile model. Petroleum Geology and Recovery Efficiency, 6, pp. 56-58, 2018.
- [40] Rashidi, M., Blokhus, A.M. and Skauge, A., Viscosity and retention of sulfonated polyacrylamide polymers at high temperatures. J. Appl. Polym. Sci., 119, pp. 3623-3629, 2011. DOI: 10.1002/app.33056.
- [41] Rashidi, M., Sandvik, S., Blokhus, A. and Skauge, A., Static and dynamic adsorption of salt tolerant polymers. In: Proceedings of the IOR 2009-15<sup>th</sup> European Symposium on Improved Oil Recovery, Paris, France, 2009. DOI: 10.3997/2214-4609.201404862.
- [42] Gramain, P. and Myard, P., Polyacrylamides with colored groups for trace analysis in water. Polymer Bulletin, 3, pp. 627-631, 1980. DOI: 10.1007/BF00285298.
- [43] Hlady, V., Lyklema, J. and Fleer, G.J., Effect of polydispersity on the adsorption of dextran on silver iodide. J. Colloid Interface Sci., 87(2), pp. 395-406, 1982. DOI: 10.1016/0021-9797(82)90336-8.
- [44] Lakatos, I., Lakatos-Szabó, J. and Tóth, J., Factors influencing polyacrylamide adsorption in porous media and their effect on flow behavior. In: Surface Phenomena in Enhanced Oil Recovery. Shah, D.O., Ed.. Springer, Boston, MA, USA. 1981. DOI: 10.1007/978-1-4757-0337-5\_37.
- [45] Herrera, J., Maya, G., et al, Experimental evaluation of the mechanical degradation of HAPM polymeric solutions used in enhanced oil recovery. CT&F - Ciencia, Tecnología y Futuro, 10(2), Special issue on EOR, pp. 131-141, 2020. DOI: 10.29047/01225383.275.
- [46] Smith, F.W., The behavior of partially hydrolyzed polyacrylamide solutions in porous media. J. Pet. Technol., 22(02), pp. 148-156, 1970. DOI: 10.2118/2422-PA.

**J.J. Herrera-Quintero**, received his BSc. Eng. in Chemical Engineering in 2009 from the Universidad Industrial de Santander, his MSc. in Engineering (Enhanced Oil Recovery) in 2018 from the Universidad Industrial de Santander. From 2009 to 2021, she worked as researcher at the Enhance Oil Recovery Laboratory Center for Innovation and Technology – ICP. Her research interests include fluids flow in porous media, enhanced oil recovery by polymer and ASP and flow control valves to polymer injection. ORCID: 0000-0002-8122-8204

**G.A. Maya-Toro**, received his BSc. Eng. in Petroleum Engineering in 2003 from the Universidad Nacional de Colombia Sede Medellín, his MSc. in Engineering (Enhanced Oil Recovery) in 2014 from the Universidad Industrial de Santander. He is a PhD (c) in Engineering from the Universidad Nacional de Colombia Sede Medellín. In 2003 and 2004, he worked for the Universidad Nacional de Colombia Sede Medellín. Since 2005 he has worked for Ecopetrol designing, executing, and evaluating enhanced and secondary oil recovery projects. His research interests include fluids flow in porous media, enhanced oil recovery, smart water, and carbon-free energy processes.

ORCID: 0000-0002-8780-3580

**K.M. Colmenares-Vargas**, holds a BSc. in Petroleum Engineering from UIS, Colombia and a MSc. in Mechanical Engineering from PUC Rio, Brazil. She has more than ten years of experience at lab and field level with projects related to IOR – EOR applications for different Ecopetrol's assets. Currently, she works at the Ecopetrol's Center for Innovation and Technology – ICP. Her research interests include lab scale evaluation of novel technologies for IOR – EOR and reservoir management. ORCID: 0000-0002-0083-7092

J.C. Vidal-Prada, received the BSc. Eng. in Chemical Engineering in 1999 from and the MSc. in Chemical Engineering in 2014, both from the

Universidad Industrial de Santander, Colombia. Currently, she works in a scientific and technologic agreement between DTH and the Center for Innovation and Technology – ICP (Piedecuesta-Santander, Colombia). His research interests include: enhanced Oil Recovery by polymer and ASP, surfactants adsorption, polymeric solutions and dispersed systems rheology. ORCID: 0000-0003-3854-7100

**D.S. Barbosa-Trillos,** received the BSc. Chemistry in 2003 from the Universidad Industrial de Santander, Bucaramanga, Colombia. MSc. Sustainable Chemistry in 2008 from the Universidad Jaume I. Castellon de la Plana, España, MSc. Environmental Engineering in 2009 and the PhD in Environmental Engineering in 2012, both from the Universidad de Murcia. Murcia, España. From 2013 to 2018, she worked for a company in the Oil & Gas sector in enhanced oil recovery projects. Currently, she works at the ECOPETROL Center for Innovation and Technology – ICP. Her research interests include sustainable chemistry, enhanced oil recovery, carbon materials nanotechnology, adsorption in porous surfaces and electrochemistry.

ORCID: 0000-0002-3335-1531

**E.O. Muñoz-Mazo** received the BSc. Eng. in Petroleum Engineering in 2002 from the Universidad Nacional de Colombia, Medellin, Colombia. MSc in Petroleum Engineering in 2005, and the PhD in Petroleum Engineering in 2013, both from the Universidade Estadual de Campinas - UNICAMP. Campinas, Brazil. From 2005 to 2018, he worked as researcher at the Reservoir Simulation and Management Laboratory – UNISIM at the Center for Petroleum Studies of UNICAMP. Currently, he works at the ECOPETROL Center for Innovation and Technology – ICP. His research interests include Reservoir simulation, Enhanced Oil Recovery, Reservoir Management and Optimization and Naturally Fractured Reservoirs. ORCID: 0000-0002-4467-2779