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EXPERIMENTAL EVALUATION OF THE MECHANICAL DEGRADATION OF HPAM POLYMERIC SOLUTIONS USED IN ENHANCED OIL RECOVERY

■ EVALUACIÓN EXPERIMENTAL DE LA DEGRADACIÓN MECÁNICA DE SOLUCIONES DE POLÍMERO HPAM, UTILIZADAS EN PROCESOS DE RECOBRO MEJORADO DE PETRÓLEO

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ABSTRACT

With the design of experiments (DoE), this study analyses the influence of physical (capillary diameter and pressure drop) and chemical variables (salinity, polymer concentration, and molecular weight) on the mechanical degradation of partially hydrolyzed polyacrylamide-type polymer solutions (HPAM) used in enhanced oil recovery processes. Initially, with the help of a fractional factorial design (2^{k-p}), the variables with the most significant influence on the polymer's mechanical degradation were found. The experimental results of the screening demonstrate that the factors that statistically influence the mechanical degradation are the molecular weight, the diameter of the capillary, and the pressure differential. Subsequently, a regression model was developed to estimate the degradation percentages of HPAM polymer solutions as a function of the significant factors influencing the mechanical degradation of polymer solutions. This model had a 97.85% fit for the predicted values under the experimental conditions. Likewise, through the optimization developed by the Box Behnken response surface methodology, it was determined that the pressure differential was the most influential factor. This variable was followed by the capillary diameter, where less than 50% degradation rates are obtained with low polymer molecular weight (6.5 MDa), pressure differentials less than 500 psi, and diameters of the capillary greater than 0.125 inches.

RESUMEN

Este estudio evaluó mediante un diseño experimental la influencia de las variables físicas (diámetro de capilar y caída de presión) y químicas (salinidad, concentración de polímero y peso molecular), en la mecánica de soluciones poliméricas tipo poliácridamidas parcialmente hidrolizadas (HPAM) utilizadas en procesos de recobro mejorado de crudo. Inicialmente, se realizó un diseño factorial fraccionado (2^{k-p}), para determinar las variables con mayor influencia sobre la degradación mecánica del polímero. Los resultados experimentales del cribado indican que los factores que influyen estadísticamente en la degradación mecánica son el peso molecular, el diámetro del capilar y el diferencial de presión. Posteriormente, se desarrolló un modelo de regresión que permite estimar los porcentajes de degradación de soluciones poliméricas HPAM en función de los factores significativos con influencia en la degradación mecánica de las soluciones poliméricas. Este modelo tuvo un ajuste del 97.85% para los valores predichos bajo las condiciones experimentales. Asimismo, mediante la optimización desarrollada por la metodología de superficie de respuesta Box Behnken, se determinó que el diferencial de presión fue el factor más influyente, seguido del diámetro del capilar, donde las tasas de degradación inferiores al 50% se obtienen con polímero de bajo peso molecular (6,5 MDa), diferenciales de presión inferiores a 500 psi y capilares con diámetros superiores a 0,125 pulgadas.

KEYWORDS / PALABRAS CLAVE

Enhanced oil recovery | polyacrylamide | HPAM | mechanical degradation | molecular weight | salinity | capillary diameter | concentration.

Recobro mejorado de aceite | poliácridamida | HPAM | degradación mecánica | peso molecular | salinidad | diámetro capilar | concentración.

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1. INTRODUCTION

Factors such as the drop in crude oil prices worldwide have allowed oil companies to develop new technologies to enhance oil recovery to improve their competitiveness. [1], [2]. Therefore, in recent years researchers and the oil industry have focused on increasing the recovery factor through enhanced oil recovery (EOR). The use of polymer injection has been one of the technologies that have allowed the increase in production in different oil fields, increasing the oil sweep efficiency [3]-[5] thanks to the improvement in the mobility relationship between polymer solution and displaced oil [6]. The most widely used polymers in enhanced recovery processes are synthetic polymers, while the best performing synthetic polymers are partially hydrolyzed polyacrylamides (HPAM) and its derivatives. Because of these polymers' low cost, the use of HPAM polymer solutions is favorable in projects for large-scale production [7], [8]. The HPAM, as other polymers, is sensitive to high shear stresses, causing rupture of the macromolecular chains, reducing their size and viscosity, and generating the mechanical degradation of the polymer [9]. These occur during the polymer preparation and

injection process, particularly in the flow regulator valves on the bottom of the reservoir [10], [11].

The previous studies have determined most of the physicochemical factors involved in the mechanical degradation of polymer solutions. However, these studies bent on the influence of these factors independently, without considering the interaction between them. For that reason, this paper aims to analyze the interaction of the physical and chemical factors that influence the mechanical degradation processes of polymeric solutions used in enhanced oil recovery. The goal is to determine the mechanical degradation of HPAM polymeric solutions through the experimental assessment in capillary tubes, considering the following factors: molecular weight, salinity, capillary diameter, concentration, and differential of pressure and, finally. Their influence is measured through a fractionated factorial design (2k-p) and a Box-Behnken design to create a response surface.

2. STATE OF TECHNIQUE

The mechanical degradation is particularly high in injection processes with high flow rates, low permeability formations, and high salinities [12]-[14]. Scientific literature results show that the degradation is more severe for high molecular weight polymers and polymer diluted solutions [11]. Furthermore, this mechanical degradation reduces polymer viscosity affecting the oil recovery, which demands greater energy consumption to carry out a homogeneous oil sweep [11]-[15]. To determine the physicochemical factors involved in the mechanical degradation of polymer solutions, different alternatives have been proposed, such as the one authored by Husveg T. et al., [16], who developed a novel valve technology for its use in EOR with polymers. By designing spiral channels adding expansion and reduction zones, greater control of shear forces is evidenced, reducing the percentage of polymer degradation. The authors demonstrated that the degradation percentage is less than 10% with pressure differentials lower than 45 bar, achieving better performance than a standard valve where the degradation percentages are between 60 and 80%. Xin X. et al. [17] evaluated the effect of polymer degradation on resilience through polymer flooding in heterogeneous reservoirs. To carry out this evaluation, they implemented a new mathematical model that allowed the design of a three-dimensional two-phase polymer injection simulator.

The static and dynamic degradation of the polymer is examined. This simulator was validated by comparing the results with a commercial simulator and with experimental results. Thanks to this simulator, it was determined that the viscosity of a polymeric solution with the same shrinkage decreases with increasing shear rate. Shear degradation was observed since the dynamic

degradation rate constant was 0.0022 day⁻¹. The static degradation rate constant was 0.0017 day⁻¹, obtaining a 7.7% decrease in oil recovery, demonstrating that polymer degradation has an adverse effect on the process efficiency. Theriot T. et al. [18] evaluated the loss of viscosity in polymer solutions by shear by the interaction of the fluid and the surface facilities of the distribution system. In this study, it was determined that the degradation of polymer solutions occurs in flow control devices. They were able to observe a direct relationship between the pressure differential and the degradation that is generated by the control device. The geometric factors and the speed have little relation with the percentage of degradation, unlike the molecular weight and the polymer structure. The polymer solution also increases its degradation between 15 and 50% when it flows through the control device with a pressure differential greater than 50 psi.

Ronin E. et al. [19] numerically evaluated the interaction of polymer solutions between mechanochemical degradation at a molecular scale and laminar flow at a macroscale, allowing to minimize the technological gap of the degradation phenomenon at a molecular scale. Duretta P & Picchioni F. [20] developed a numerical model that estimates the efficiency of oil recovery in the reservoir by comparatively evaluating recovery using water and polymer solution. It is estimated 30% more recovery using polymers. Al Hashmi A.R. et al. [9] analyzed the degradation of polymeric solutions, with partially hydrolyzed polyacrylamides (HPAM), through capillaries. They determined that the degradation increased with shear stresses above 15,000 s⁻¹ due to the shear effect occurring on the capillary bulb's shoulder.

3. EXPERIMENTAL DEVELOPMENT

POLYMER USED AND WATER COMPOSITION

Three polymers of the partially hydrolyzed polyacrylamide type (HPAM) were used. These are anionic and are of three different molecular

weights. Table 1 describes the polymer molecules used and some of their chemical characteristics. The polymers were prepared in three different synthetic sodium chloride brine corresponding to 500, 2,500, and 4,500 mg / L of NaCl to evaluate the salinity effects.

Table 1. Composition of the studied polymers.

Polymer	% Acrylamide	% Acrylate	% Hydrolysis	Molecular weight (MDa)
A	66.2	33.8	25-30	6.5
B	67.2	32.8	25-30	12.5
C	72.2	27.8	25-30	18.5

PREPARATION OF THE POLYMER SOLUTION

The stock solution has been prepared according to API RP63 standard [21], at a concentration of 5,000 ppm, by slowly adding the polymer powder to the vortex formed by the preparation water with adequate mechanical stirring. The polymer is stirred until completely dissolved. The final solution used is obtained from diluting the stock solution with the preparation water at polymer concentrations of 500, 1,500, and 2,000 ppm.

MEASUREMENT AND DATA ACQUISITION.

Figure 1 illustrates the assembly of the equipment for the acquisition of experimental data. The procedure applied, which is explained next, was based on the API RP63 standard [21]. Following the preparation of the polymeric solution, the initial viscosity (n_o) measurement is carried out at ambient temperature. The diluted solution is introduced through the upper part of the steel cylinder, and then the lid was placed with the respective capillary to evaluate. Later, employing the nitrogen regulating valves, the pressure to assess mechanical degradation is adjusted. The polymer solution is next flowed through the reduced diameter capillary to cause shear stress. The time it takes for a mass greater than 50 g of the polymer solution to pass from the first drop that exits the capillary is measured. The time, as well as the weight reached, are recorded. Equation 1 presents the shear rate formula.

$$\dot{\gamma}_a = \frac{4 Q}{\pi R^3} \quad (1)$$

Where $\dot{\gamma}_a$ is the shear stress, Q the flow rate, R the internal radius of the capillary used [22]. Lastly, the viscosity of the degraded solution is measured n_{deg} .

DETERMINATION OF THE VISCOSITY DEGRADATION RATE.

The Brookfield LVT viscometer with ULA adapter or Din 86 measured the viscosity of the samples. A temperature controller was used to secure homogeneous measurement conditions in a suitable range for the analyzed samples, determining the viscosity at a shear stress of 7.3 s^{-1} @ $30 \text{ }^\circ\text{C}$. The degradation percentage of the samples was determined by measuring the viscosity: initial of the non-degraded solution (n_o), the degraded solution (n_{deg}), and the solvent or synthetic water for preparation (n_s), as shown in Equation 2 [9].

$$\% \text{ Deg} = \frac{n_o - n_{deg}}{n_o - n_s} * 100 \quad (2)$$

EXPERIMENTAL CONDITIONS

The fractional factorial design (2kp) implanted identifies significant process parameters, applying a 5-factor degradation screening with

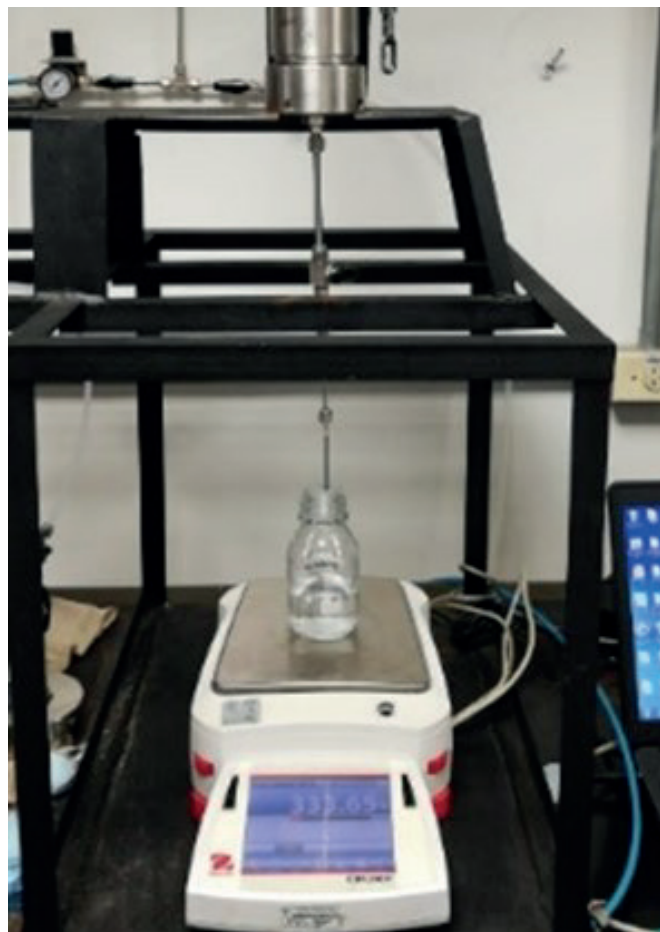


Figure 1. Assembly of equipment for assessing the degradation of the polymeric solution.

two levels (25-1). Then, through a response surface methodology (RSM), a regression model was found that enables the estimation of polymeric solutions degradation according to variables (molecular weight (MDa), salinity in NaCl equivalents (ppm), capillary diameter (in), concentration (ppm), ΔP (psi)). For the RSM, a Box-Behnken (BBD) design is employed with three central points to increase the error-free level.

FRACTIONAL FACTORIAL DESIGN (2KP)

Table 2 shows the experimental fractional factorial design of 5 factors with two levels (25-1). The chemical factors involved in this design, such as molecular weight, salinity, and polymer concentration, are variables that directly affect the viscosity of the polymeric solution. According to the literature, the degradation rate and the physical factors with the most weight correspond to the orifice diameter and the differential pressure. The range of high and low levels is currently used in pilot processes or expanding polymer injection technologies. In this phase, the polymeric solutions of low and high molecular weights of 6.5 MDa and 18.5 MDa, respectively, charged the injection cylinder. The salinity varied between 500 ppm and 4,500 ppm, and the concentration between 500 ppm and 2,500 ppm. The capillary diameter was minimum 1/16 inches and maximum 1/4 inches, and the differential pressure was 200 psi (min.) and 800 psi (max.), respectively.

Table 2. Fractionated Factorial design.

Factors	Variable	Low level [-1]	High level [1]
Molecular weight (MDa)	A	6.5	18.5
Salinity in NaCl (ppm) equivalents	B	500	4,500
Capillary diameter (in)	C	1/16	1/4
Concentration (ppm)	D	500	2,500
ΔP (psi)	E	200	1,400

BOX-BEHNKEN DESIGN (BBD)

The previous stage's fractional factorial experiment enables determining the most significant factors in the HPAM polymer solution degradation rate. A second experimental stage, which consists of a Box-Behnken experimental design (2^k) with three central points, as shown in Table 3, enables the development of a response surface. In this second stage, the polymeric solutions (500 ppm) for each experimental condition were prepared with a salinity of 500 ppm as fixed factors. The molecular weight varied between 6.5 MDa and 18.5 MDa as low and high levels, respectively, with central points of 12.5 MDa as medium level. The differential pressure ranges between 200 psi and 800 psi, with central points of 500 psi as medium level. Finally, the capillary diameter varied between 1/16 and 1/4 inches, with 1/8 inches as central point.

Table 3. Box-Behnken design.

Factors	Variable	Low level [-1.0]	Medium level [0.0]	High level [1.0]
Molecular weight (MDa)	A	6.5	12.5	18.5
Capillary diameter (in)	B	1/16	1/8	1/4
ΔP (psi)	C	200	500	800

Table 4. Results of the screening experimentation.

Run	Molecular weight (MDa)	Salinity (ppm)	Capillary diameter (in)	Concentration (ppm)	Delta P (psi)	Degradation rate (%Dr)
1	6.5 (-1)	500 (-1)	1/16 (-1)	500 (-1)	200 (-1)	30.03
2	18.5 (1)	500 (-1)	1/16 (-1)	500 (-1)	1,400 (1)	76.95
3	6.5 (-1)	4,500 (1)	1/16 (-1)	500 (-1)	1,400 (1)	50.68
4	18.5 (1)	4,500 (1)	1/16 (-1)	500 (-1)	200 (-1)	57.41
5	6.5 (-1)	500 (-1)	1/4 (1)	500 (-1)	1,400 (1)	53.00
6	18.5 (1)	500 (-1)	1/4 (1)	500 (-1)	200 (-1)	39.93
7	6.5 (-1)	4,500 (1)	1/4 (1)	500 (-1)	200 (-1)	20.28
8	18.5 (1)	4,500 (1)	1/4 (1)	500 (-1)	1,400 (1)	74.64
9	6.5 (-1)	500 (-1)	1/16 (-1)	2,500 (1)	200 (-1)	7.83
10	18.5 (1)	500 (-1)	1/16 (-1)	2,500 (1)	1,400 (1)	22.77
11	6.5 (-1)	4,500 (1)	1/16 (-1)	2,500 (1)	1,400 (1)	56.30
12	18.5 (1)	4,500 (1)	1/16 (-1)	2,500 (1)	200 (-1)	8.59
13	6.5 (-1)	500 (-1)	1/4 (1)	2,500 (1)	1,400 (1)	36.56
14	18.5 (1)	500 (-1)	1/4 (1)	2,500 (1)	200 (-1)	9.36
15	6.5 (-1)	4,500 (1)	1/4 (1)	2,500 (1)	200 (-1)	20.93
16	18.5 (1)	4,500 (1)	1/4 (1)	2,500 (1)	1,400 (1)	58.97

Subsequently, to determine the optimal conditions of the polymeric solutions degradation percentage, a regression model was built, and a statistical optimization process using R-Studio® was carried out. The regression model obtained was developed following the structure shown in Equation 3:

$$Y = \beta_0 + \sum_{i=1}^{i=3} \beta_i x_i + \sum_{j=2}^{j=3} \sum_{i=1}^{i=2} \beta_{ij} x_i x_j + \sum_{i=1}^{i=3} \beta_{ii} x_i^2 + \varepsilon \quad (3)$$

Where Y is the response of the regression model, x_i and x_j are the experimental process factors, β_0 is the intersection term, β_i is the coefficient of the linear terms, β_{ij} set the coefficients of the interaction terms between factors, β_{ii} is the coefficient of the quadratic terms, and ε is the modeling error term. The model fit was determined using the analysis of the lack of fit and the Durbin-Watson tests. Similarly, the residual structure was analyzed, as well as the standard R^2 and the adjusted R_{adj}^2 coefficients to determine the model fitting level.

4. RESULTS

FRACTIONED FACTORIAL DESIGN (2^{k-P}) RESULTS

In the fractionated factorial design (25-1), 16 experiments were carried out. Table 4 shows the experimental results for the degradation rate. The HPAM polymer solution presents a mechanical degradation rate that fluctuates between 7.83% corresponding to experiment 11 and 76.95% in experiment 2.

BOX BEHNKEN DESIGN RESULTS

The experimental results showed that the polymeric solutions present mechanical degradation ranging between 22.0% and

Table 5. Results for the Box-Behnken response surface experiment.

Run	Molecular weight	Capillary diameter	Delta P	Degradation rate	Degradation rate *	Relative error
	(MDa)	(in)	(psi)	(%)	(%)	(%)
1	18.5(1)	1/16 (-1)	500 (0)	68.22	69.27	1.54
2	6.5 (-1)	1/8 (0)	800 (1)	67.67	68.46	1.17
3	6.5 (-1)	1/16 (-1)	500 (0)	54.08	55.85	3.27
4	12.5 (0)	1/8 (0)	500 (0)	66.60	69.47	4.31
5	12.5 (0)	1/8 (0)	500 (0)	70.51	69.47	1.47
6	12.5 (0)	1/8 (0)	500 (0)	68.55	69.47	1.34
7	18.5(1)	1/8 (0)	200 (-1)	54.23	53.3	1.71
8	18.5(1)	1/8 (0)	800 (1)	81.19	81.88	0.85
9	12.5 (0)	1/4 (1)	200 (-1)	22.07	27.46	24.42
10	6.5 (-1)	1/4 (1)	500 (0)	45.62	43.63	4.36
11	6.5 (-1)	1/8 (0)	200 (-1)	43.20	39.88	7.69
12	12.5 (0)	1/16 (-1)	800 (1)	69.92	68.26	2.37
13	12.5 (0)	1/4 (1)	800 (1)	55.86	56.04	0.32
14	18.5(1)	1/4 (1)	500 (0)	60.64	57.05	5.92
15	12.5 (0)	1/16 (-1)	200 (-1)	40.82	39.68	2.79
Relative error mean						4.24

Degradation rate *: Statistical model

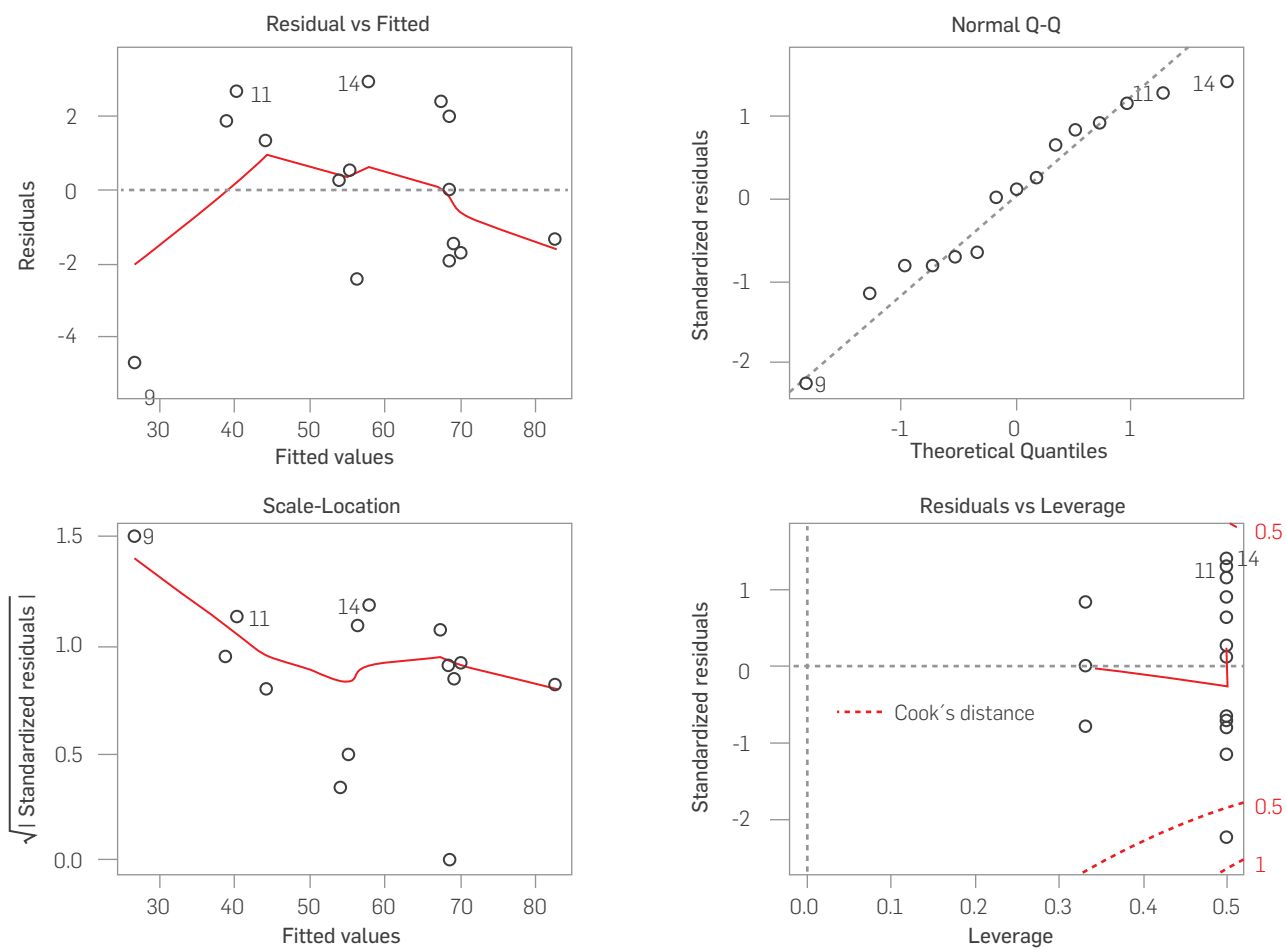


Figure 2. Evaluation of statistical assumptions.

81.2%. These mechanical degradation results involve the following three experimental factors: molecular weight, capillary diameter, and delta P (pressure drop). Table 5 shows the values obtained experimentally in each condition of Table 3, along with the predetermined values for the polynomial equation (Equation 4) and its relative errors

STATISTICAL RESULTS

To determine the experimental analysis reliability, all statistical diagnoses were assessed, obtaining favorable results and showing that all the assumptions were achieved with the following results. The lack of fit observed was not significant. Also, the residual behavior was analyzed to verify the validity of the experiment. Figure 2 shows the graphs of independence, the normal probability plot, and the homoscedasticity plot of the residues obtained for the response surface experiment.

Figure 3 shows no evidence of abnormal behavior of the obtained residues and, thus, the normality assumptions in the response surface experiment are validated. Comparing the residual value's dispersion ranges at the different factor levels, we validated the homoscedasticity criteria. As verification of self-correlation, the Durbin-Watson statistic was calculated, with a value of 1.76682 and a p-value equal to 0.1958. Thus, confirming the absence of correlation between residues.

5. RESULTS ANALYSIS

ANALYSIS OF THE SCREENING EXPERIMENT

The analysis of variance (ANOVA) with a confidence level of 95% determined the statistical significance of each factor on the mechanical degradation of the HPAM polymer solutions. The p-value reveals the relevance of each element, where values below 0.05

show each factor's significance and their second-order interactions. As shown in Table 6, the analysis of variance (ANOVA) displayed that the effects of the main factors, A, C, and E, are the ones that have the most influence on the mechanical degradation of the HPAM polymer solutions.

Due to the alias structure in the fractionated factorial design, the main effects of B and D have a close relationship with factor A. Based on the hierarchical categorization principle, the first-order factors and the second-order interactions have more relevance and more probability of statistical influence on the response variable. It was, therefore, as seen in figure 3, determined that the factors with the highest impact on the mechanical degradation of the HPAM polymeric solutions were the molecular weight (A), the capillary diameter (C), and the delta P (E).

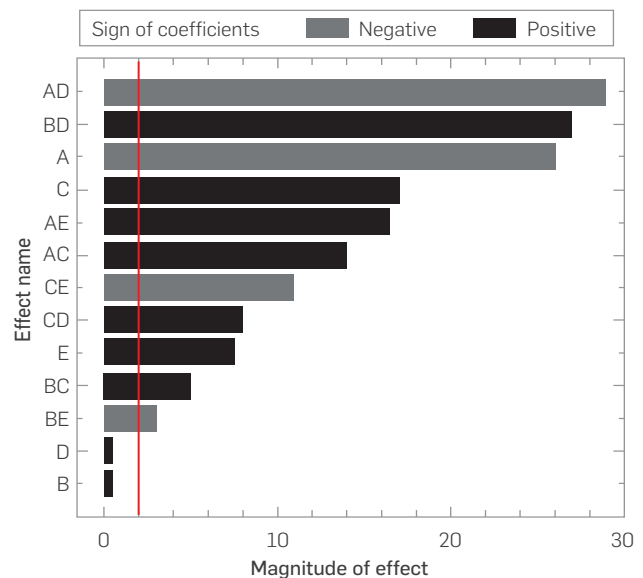


Figure 3. Pareto chart for the effects of each factor.

Table 6. Results of the analysis of variance (ANOVA) for the screening experiment.

Source	Sum of squares	Degrees of freedom	Middle Square	F-value	p-value
A: Molecular weight	537.723	1	537.723	73.89	0.0133
B: Salinity	518.201	1	518.201	7.12	0.1164
C: Capillary diameter	488.689	1	488.689	67.15	0.0146
D: Concentration	503.938	1	503.938	6.92	0.1191
E: Delta P	248.931	1	248.931	34.21	0.0280
AC	445.895	1	445.895	61.27	0.0159
AD	1,156.24	1	1156.24	158.88	0.0062
AE	453.806	1	453.806	62.36	0.0157
BC	247.305	1	247.305	33.98	0.0282
BD	635.493	1	635.493	87.32	0.0113
BE	158.423	1	158.423	21.77	0.0430
CD	307.576	1	307.576	42.26	0.0229
CE	329.31	1	329.31	45.25	0.0214
Total error	145.548	2	727.741		
Total (corr.)	7,883.0	15			

ANALYSIS OF THE RESPONSE SURFACE EXPERIMENT

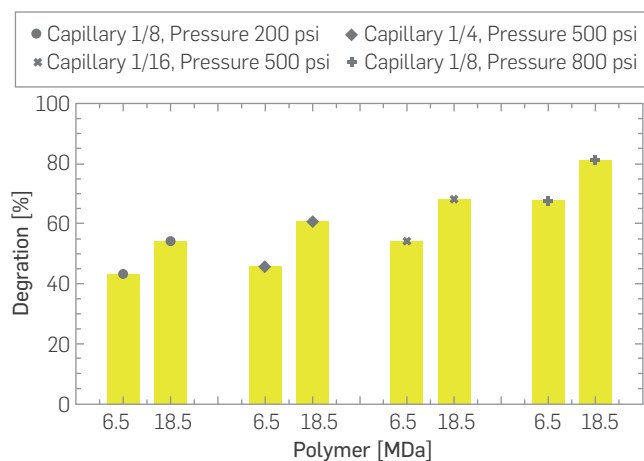
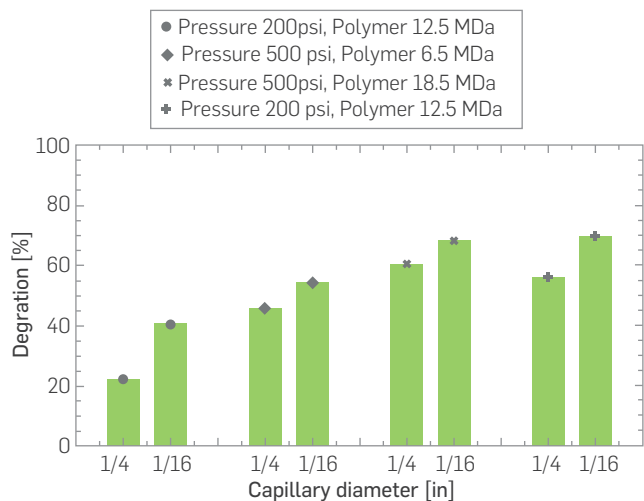
Table 7 presents the ANOVA, where the main factors (A, B, and C) and the second-order interactions (BB and CC) are statistically significant, with a 95% reliability level, on the mechanical degradation of the polymeric solutions. Similarly, the other second-order interactions are not substantial, but they were maintained in the analysis to fit the regression model better. Based on the results, the pressure delta (C) was the factor that had the most statistically significant effect on the mechanical degradation of the HPAM polymeric solutions, with a p-value of 0.0001.

MOLECULAR WEIGHT

Figure 4 compares various scenarios with the same capillary diameter and pressure but with different molecular weight. The

Table 7. Initial ANOVA for the response surface experiment.

Source	Sum of squares	Degrees of freedom	Middle Square	F-value	p-value
A: Molecular weight	349.261	1	349.261	30.86	0.0026
B: Capillary diameter	298.313	1	298.313	26.36	0.0037
C: Delta P	1,609.29	1	1,609.29	142.18	0.0001
AA	8.26497	1	8.26497	0.73	0.4318
AB	0.643854	1	0.643854	0.06	0.8210
AC	1.55829	1	1.55829	0.14	0.7258
BB	415.381	1	415.381	36.70	0.0018
BC	10.3045	1	10.3045	0.91	0.3838
CC	265.272	1	265.272	23.44	0.0047
Total error	56.5926	5	11.3185		
Total (corr.)	3,219.51	14			

**Figure 4.** Behavior of the degradation percentage when comparing the molecular weight for the various conditions evaluated.**Figure 5.** Behavior of the percentage of degradation when comparing the capillary diameter for the various conditions assessed.

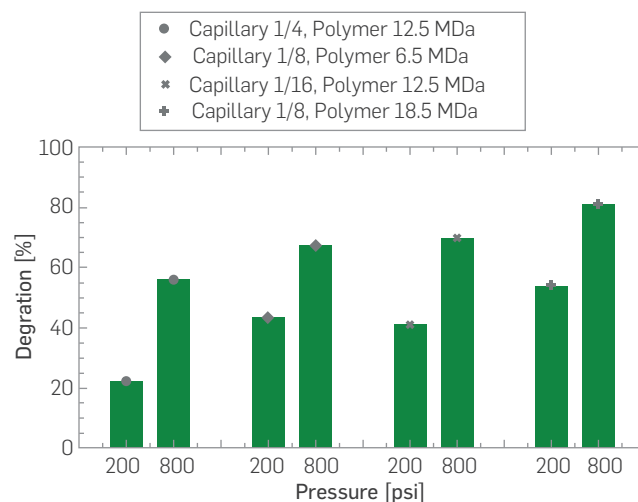
results show that, in all cases, the highest degradation rate is in the HPAM polymer with the highest molecular weight (18.5 MDa). Furthermore, it exposes an increasing trend in the rate of degradation with pressure, regardless of the capillary diameter

CAPILLARY DIAMETER

Regarding the degradation rate as a function of the capillary diameter (Figure 5), the capillary with the smallest diameter (1/16 inches) is the one that generates the highest rate of degradation. For all the scenarios where the pressure and molecular weight are equal, the 1/16 inches diameter produces higher percentages of degradation than the 1/4 inches diameter.

PRESSURE

The experimental data with the same capillary diameter, same polymer, and different pressures allow us to observe that, compared to the previous graphs, the pressure change is the variable with the most significant influence on the degradation rate. For all the cases shown in Figure 5, the differences in degradation rates for pressures of 200 and 800 psi are higher than 20%.

**Figure 6.** Behavior of the degradation percentage when comparing the pressure delta for the various conditions assessed.

OPTIMIZATION BY RESPONSE SURFACE

With the data obtained in the response surface experiment, a regression model was adjusted; this model is shown in Equation 4. According to the significant interaction between factors, a quadratic structure was used for this model and the R² of the resulting model was 0.9785. Table 8 shows the coefficients of the regression model.

$$\%Dr = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 B^2 + \beta_5 C^2 \quad (4)$$

Where A is molecular weight, B is capillary diameter, and C is pressure differential.

Table 8. Coefficients of the regression model.

Coefficient	Estimated
β_0	69.47
β_1	6.71
β_2	-6.11
β_3	14.29
β_4	-13.02
β_5	-8.59

As observed in figure 7, the regression model achieves a proper match with the predicted data in the expression obtained in equation 4. Similarly, with this model, response surfaces identify operating regions with less mechanical degradation of the polymeric solutions in proven experimentation regions.

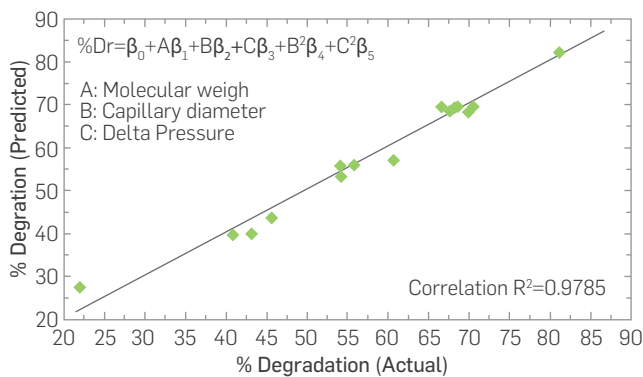
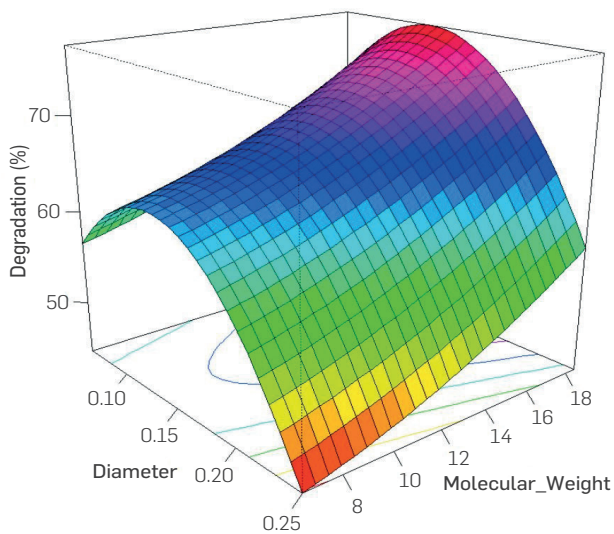
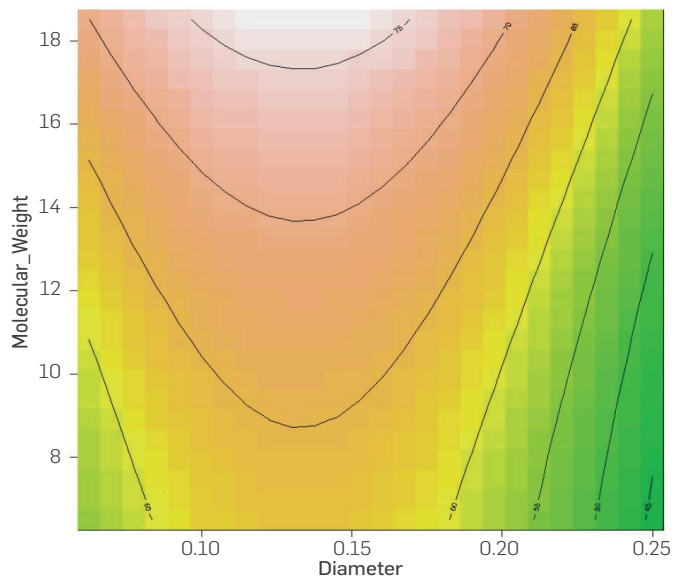


Figure 7. Response surface for degradation as a function of capillary diameter vs. molecular weight, with pressure differential equal to 500 psi.



Slice at Pressure = 500, Length = 0, Class = Null, Mode = NULL

(a)



Slice at Pressure = 500

(b)

Figure 8. Response surface for degradation as a function of capillary diameter vs. molecular weight, with pressure differential equal to 500 psi

Figure 8 shows the mechanical degradation rates of HPAM polymer solutions when the pressure differential is 500 psi, but the diameter of the capillary and the molecular weight (MW) changes. The observed behavior shows that the higher the MW, the greater the polymer degradations, confirming what the literature reported [11], having a considerable influence on the polymer's degradation, together with the diameter of the capillary.

As shown in figure 9, the high rates of polymer degradation occur when the cross-section of the flow is lower, thus increasing the shear stresses on the molecular chain and reducing the viscosity substantially. In Figure 9b, the degradation is <45%, with diameters less than 0.15 inches and a minimum pressure drop of 200 psi. Additionally, there are near degradation values between diameters of 0.1 and 0.15 inches, which can be related to the acceptance criterion of 5% of the p-value; the contour lines of the surface demonstrate this behavior.

Figure 10 shows the significant effect of pressure on the degradation rate. At forces higher than 500 psi, degradations rates over 60% are reached regardless of whether it has a low or high molecular weight. Moreover, at pressures below 500 psi, the degradation of the polymer is more significant when the MW exceeds 14 MDa. The previous results were analyzed, keeping the capillary diameter fixed at 1/8 inches.

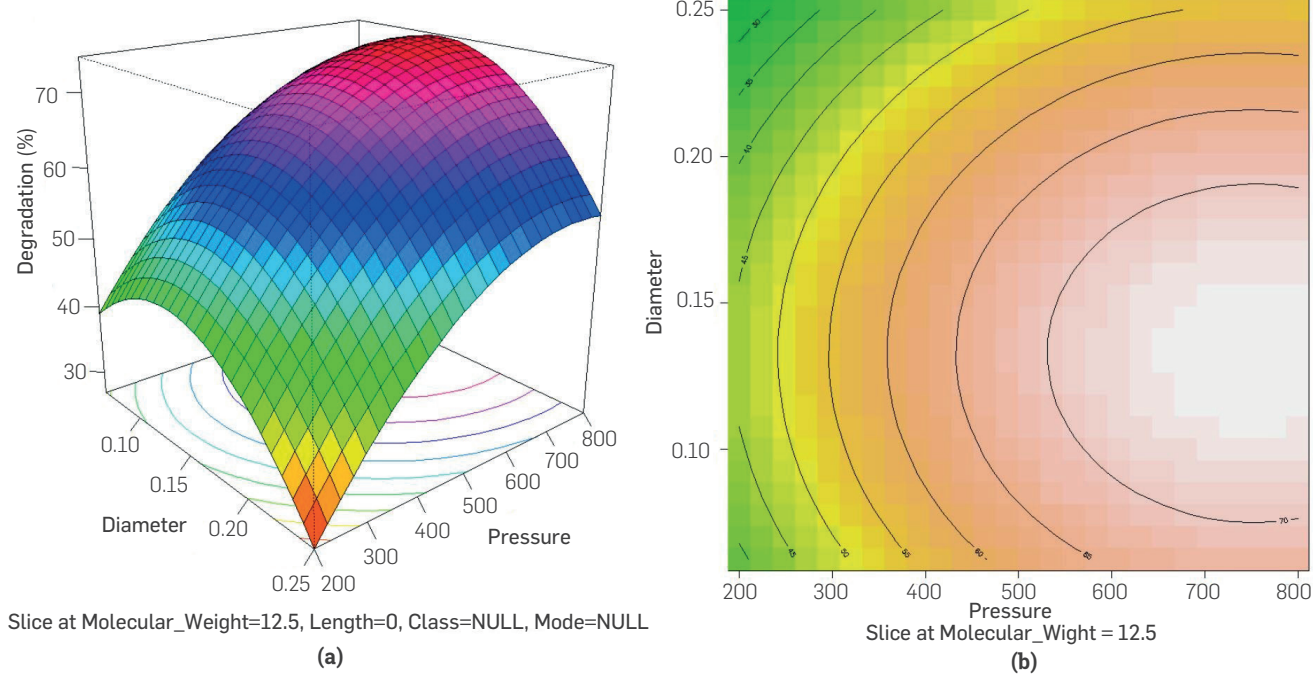


Figure 9. Response surface for degradation as a function of capillary diameter vs. pressure differential, with molecular weight equal to 12.5 MDa.

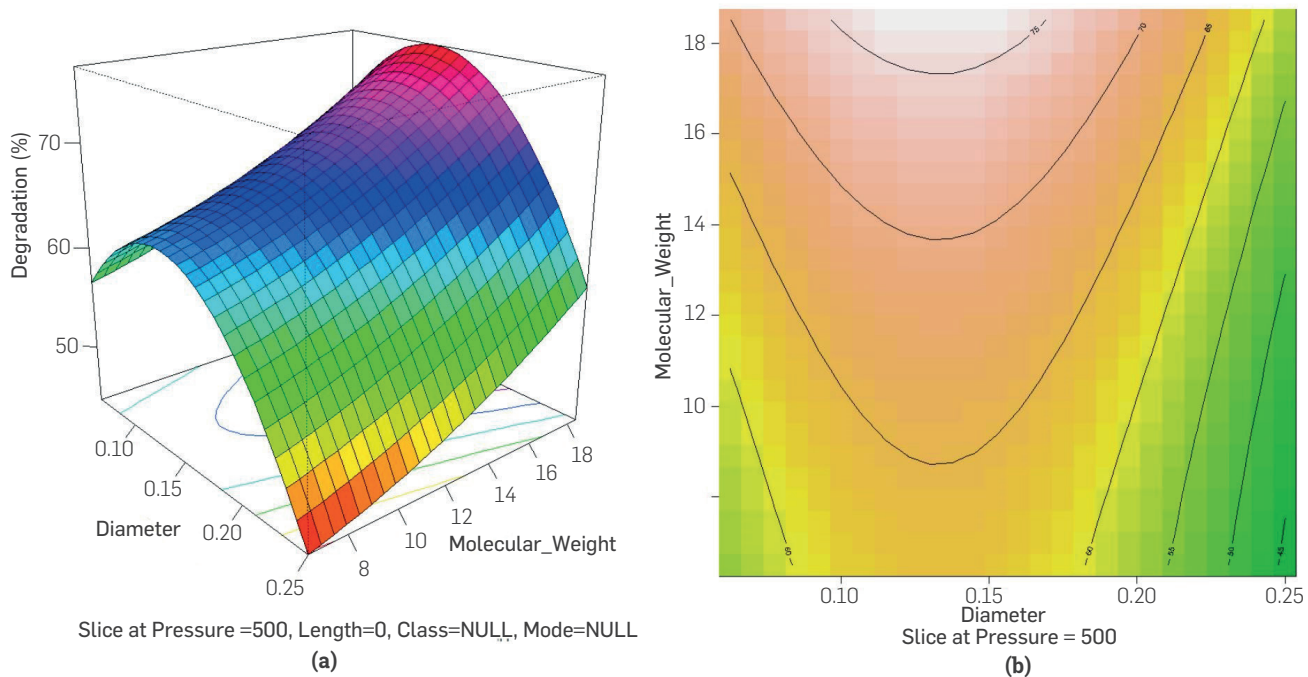


Figure 10. Response surface for degradation as a function of molecular weight vs. pressure differential, with a capillary diameter equal to 1/8 inches.

CONCLUSIONS

This work shows that the factors with the most significant influence on the mechanical degradation of polymeric solutions are the molecular weight, the capillary diameter, and the pressure differential. Where the pressure differential is the most influential with a P-Value of (0.0001). This is mainly because the capillary diameter and the pressure differential are highly related to the shear stresses to which the polymer is subjected, being fundamental factors in the fluids' continuity. It was also observed that the higher the molecular weight of HPAM, the greater the loss of viscosity. In contrast, the diameter of the capillary indicates an inversely proportional behavior, where for smaller diameters, higher degradation percentages were found.

The pressure drops, together with the abrupt reduction in the cross-sectional part of the capillary, give rise to a rupture in the molecules

due to the extensional forces acting thereon. This is consistent with the response surfaces for the highest degradation rate values are in the scenarios with the highest pressure differential and molecular weight and the smallest capillary diameters. Additionally, the response surfaces show degradation rates lower than 50% in cases of low molecular weight polymer (6.5 MDa), pressure differentials between 200 and 500 psi, and capillary diameters greater than 0.125 inches. With these results, it can be considered that the regression model developed is a useful tool to estimate the degradation percentages of the HPAM polymeric solution where the molecular weight, the diameter of the capillary, and the flooding pressure differential are known, with a mean statistical error of less than 4%. This regression model allows predicting degradation rate values in short times and with good approximations, beneficial when the loss of viscosity in CEOR processes can be mitigated, from polymer solution preparation facilities to its flow in the reservoir.

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REFERENCES

- [1] H. Zhong, Y. Li, W. Zhang, H. Yin, J. Lu, and D. Guo, "Microflow Mechanism of Oil Displacement by Viscoelastic Hydrophobically Associating Water-Soluble Polymers in Enhanced Oil Recovery," *Polymers (Basel)*, vol. 10, no. 6, p. 628, Jun. 2018. <https://doi.org/10.3390/polym10060628>.
- [2] M. Khalil, B. M. Jan, C. W. Tong, and M. A. Berawi, "Advanced nanomaterials in oil and gas industry: Design, application and challenges," *Appl. Energy*, vol. 191, pp. 287–310, Apr. 2017. <https://doi.org/10.1016/j.apenergy.2017.01.074>
- [3] P. Druetta and F. Picchioni, "Branched polymers and nanoparticles flooding as separate processes for enhanced oil recovery," *Fuel*, vol. 257, p. 115996, Dec. 2019. <https://doi.org/10.1016/j.fuel.2019.115996>
- [4] A. Mohsenatabar Firozjahi and H. R. Saghafi, "Review on chemical enhanced oil recovery using polymer flooding: Fundamentals, experimental and numerical simulation," *Petroleum*, Sep. 2019. <https://doi.org/10.1016/j.petlm.2019.09.003>
- [5] N. Khan et al., "Experimental and mechanism study: Partially hydrolyzed polyacrylamide gel degradation and deplugging via ultrasonic waves and chemical agents," *Ultrason. Sonochem.*, vol. 56, pp. 350–360, Sep. 2019. <https://doi.org/10.1016/j.ultsonch.2019.04.018>
- [6] L. M. Corredor, M. M. Husein, and B. B. Maini, "A review of polymer nanohybrids for oil recovery," *Adv. Colloid Interface Sci.*, vol. 272, p. 102018, Oct. 2019. <https://doi.org/10.1016/j.cis.2019.102018>
- [7] J. J. Sheng, B. Leonhardt, and N. Azri, "Status of Polymer-Flooding Technology," *J. Can. Pet. Technol.*, vol. 54, no. 02, pp. 116–126, Mar. 2015. <https://doi.org/10.2118/174541-PA>
- [8] A. M. Mansour, R. S. Al-Maamari, A. S. Al-Hashmi, A. Zaitoun, and H. Al-Sharji, "In-situ rheology and mechanical degradation of EOR polyacrylamide solutions under moderate shear rates," *J. Pet. Sci. Eng.*, vol. 115, pp. 57–65, Mar. 2014. <https://doi.org/10.1016/j.petrol.2014.02.009>
- [9] A. R. Al Hashmi, R. S. Al Maamari, I. S. Al Shabibi, A. M. Mansoor, A. Zaitoun, and H. H. Al Sharji, "Rheology and mechanical degradation of high-molecular-weight partially hydrolyzed polyacrylamide during flow through capillaries," *J. Pet. Sci. Eng.*, vol. 105, pp. 100–106, May 2013. <https://doi.org/10.1016/j.petrol.2013.03.021>
- [10] D. C. Morel, S. Jouenne, M. VERT, and E. Nahas, "Polymer Injection in Deep Offshore Field: The Dalia Angola Case," in *SPE Annual Technical Conference and Exhibition*, 2008. <https://doi.org/10.2118/116672-MS>
- [11] A. Zaitoun, P. Makakou, N. Blin, R. S. Al-Maamari, A.-A. R. Al-Hashmi, and M. Abdel-Goad, "Shear Stability of EOR Polymers," *SPE J.*, vol. 17, no. 02, pp. 335–339, Jun. 2012. <https://doi.org/10.2118/141113-PA>
- [12] J. M. Maerker, "Mechanical Degradation of Partially Hydrolyzed Polyacrylamide Solutions in Unconsolidated Porous Media," *Soc. Pet. Eng. J.*, vol. 16, no. 04, pp. 172–174, Aug. 1976. <https://doi.org/10.2118/5672-PA>
- [13] M. Moan and A. Omari, "Molecular analysis of the mechanical degradation of polymer solution through a porous medium," *Polym. Degrad. Stab.*, vol. 35, no. 3, pp. 277–281, Jan. 1992. [https://doi.org/10.1016/0141-3910\(92\)90036-5](https://doi.org/10.1016/0141-3910(92)90036-5)
- [14] Y. Wu, A. Mahmoudkhani, P. Watson, T. R. Fenderson, and M. Nair, "Development of New Polymers with Better Performance under Conditions of High Temperature and High Salinity," in *SPE EOR Conference at Oil and Gas West Asia*, 2012. <https://doi.org/10.2118/155653-MS>
- [15] P. Druetta, P. Raffa, and F. Picchioni, "Chemical enhanced oil recovery and the role of chemical product design," *Appl. Energy*, vol. 252, p. 113480, Oct. 2019. <https://doi.org/10.1016/j.apenergy.2019.113480>
- [16] T. Husveg et al., "The Development of a Low-Shear Valve Suitable for Polymer Flooding," *Society of Petroleum Engineers*, vol. 25, p. 2632–2647, Mar. 2020. <https://doi.org/10.2118/201223-PA>
- [17] Xin, X., Yu, G., Chen, Z., Wu, K., Dong, X., Zhu, Z.: Effect of polymer degradation on polymer flooding in heterogeneous reservoirs. *Polymers (Basel)* 10, 1–25 (2018). <https://doi.org/10.3390/polym10080857>.
- [18] T. P. Theriot, H. Linnemeyer, D. Alexis, T. Malik, and C. Perdue, "Evaluation of viscosity loss of viscosified brine solutions due to shear degradation in distribution system components," *Proc. - SPE Symp. Improv. Oil Recover.*, vol. 2018-April, 2018. <https://doi.org/10.2118/190178-MS>
- [19] E. Rognin, N. Willis-Fox, T. A. Aljohani, and R. Daly, "A multiscale model for the rupture of linear polymers in strong flows," *J. Fluid Mech.*, vol. 848, pp. 722–742, 2018. <https://doi.org/10.1017/jfm.2018.411>
- [20] P. Druetta and F. Picchioni, "Influence of the polymer degradation on enhanced oil recovery processes," *Appl. Math. Model.*, vol. 69, pp. 142–163, 2019. <https://doi.org/10.1016/j.apm.2018.11.051>
- [21] American Petroleum Institute, "Recommended practices for evaluation of polymers used in enhanced oil recovery operations," Washington, 1990.
- [22] F. A. Morrison, *Understanding Rheology*, Oxford University Press. Vol. 1. 2001.

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NOMENCLATURE

$\dot{\gamma}_a$	Shear rate
Q	Flow rate
R	Internal radius
n_o	Initial viscosity
n_s	Solvent viscosity
n_{deg}	Degraded solution viscosity
x_i, x_j	Experimental process factors
β_0	Intersection term
β_i	coefficients of the linear terms
β_{ij}	coefficients of the interaction terms between factors
β_{ii}	coefficients of the quadratic terms
ε	modeling error term
(R^2)	determination coefficients
(R^2_{adj})	(adjusted determination coefficients)