

Optimization of enhanced oil recovery using ASP solution

Landson Soares Marques^{a,*}, Pamela Dias Rodrigues^b, George Simonelli^a,
Denilson de Jesus Assis^c, Cristina M. Quintella^b, Ana Katerine de Carvalho Lima
Lobato^{a,c}, Olívia Maria Cordeiro de Oliveira^d, Luiz Carlos Lobato dos Santos^a

^a Oil, Gas, and Biofuels Research Group (PGBio), Postgraduate Program of Chemical Engineering (PPEQ), Federal University of Bahia (UFBA), R. Prof. Aristides Novis, 2, 2^o floor, Federação, CEP 40210-630, Salvador, BA, Brazil

^b Institute and Center for Energy and Environment (CIENAM), Federal University of Bahia (UFBA), R. Av. Adhemar de Barros, s/n, 2^o floor, Ondina, CEP 40301-110, Salvador, BA, Brazil

^c Engineering School, Salvador University (UNIFACS), Av. Tancredo Neves, 2131, Caminho das Árvores, CEP 40231-902, Salvador, BA, Brazil

^d Postgraduate Program of Geochemistry, Federal University of Bahia (UFBA), R. Av. Adhemar de Barros, s/n, 2^o floor, Ondina, CEP 40301-110, Salvador, BA, Brazil

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ABSTRACT

Many studies have been conducted to focused on developing an optimal alkali/surfactant/polymer (ASP) composition to increase the recovered fraction of oil in reservoirs that have already undergone water injection. To analyze the effect of alkali (Na_2CO_3), surfactant (lauryl sodium sulfate), and polymer (commercial xanthan gum) concentration on oil recovery, a complete factorial experimental design was performed with combinations of three variables (alkali, surfactant, and polymer) and three central point replications ($2^3 + 3$). The experiments were carried out on a core holder using rock samples from the Botucatu formation. The simulated oil reservoirs have an average permeability of 348 mD and a temperature of 60 °C. The crude oil was acquired from the Carmópolis field, with 25.72 °API. Synthetic production water containing 40,000 mg L⁻¹ of NaCl and 13,000 mg L⁻¹ of Na₂SO₄ was injected through an HPLC pump to saturate the rock samples and to recover the oil in the secondary step. From the experimental results, it was verified that the surfactant and polymer concentrations are the most statistically significant independent variables and that first-order interactions are not statistically significant for the process. The oil recovery factors in the secondary stage ranged between 30 and 36 % of the OOIP, which are within the range reported in the literature. The optimal composition of the ASP fluid obtained a recovered fraction of oil of 62 % in the advanced step. Other combinations reported in the literature used higher concentrations of alkali, surfactant, and polymer with lower recoveries and higher cost in the injection design. Thus, the present study highlights the necessity to investigate the performance of each component of the ASP solution. In addition, the results obtained in this study are very attractive for possible full-scale applications.

1. Introduction

The chemical methods used in advanced petroleum recovery (EOR) processes, such as the injection of alkali, low salinity water, a

* Corresponding author.

E-mail address: Landson.soares@gmail.com (L.S. Marques).

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Table 1

Key screening criteria for ASP injection [19].

EOB	Oil gravity (°API)	Viscosity (cP)	Oil saturation (%)	Formation type	Average permeability (mD)	Average porosity (%)	Temperature (°C)
ASP Solution	>20	<100	>20	Sandstone	>100	>20	<70

surfactant, foam, or polymer, are more widely used than thermal, miscible, and other methods [1]. The literature presents several strategies to improve the performance of individual techniques, such as alkali-associated surfactant, alkali-associated polymer, polymer-associated surfactant, and alkali, surfactant, and polymer (ASP) injection [2].

The ASP process is based on the injection of an aqueous solution containing an alkaline substance, surfactant, and polymer. Alkaline substances and surfactants aim to reduce the interfacial tension (IFT) between the displacing and displaced fluids, thereby increasing the displacement efficiency and reducing residual oil saturation after injection [3]. However, this process causes an increase in the effective permeability to water, which results in a more unfavorable mobility ratio inside the rock, therefore necessitating the injection of a polymer. The presence of the polymer contributes to reducing the mobility ratio between the displacing and displaced fluids and increases the sweeping efficiency [4].

The solution containing the alkali reacts with the organic acids present in the oil and produce surfactant in situ, which lowers the fluid IFT with the oil to extremely low values [5]. It has been reported that the lowest IFT are achieved using low concentration alkali solutions. However, the demand for the consumption of the reservoir mandates the use of alkali solutions with concentrations above those reported in laboratory-scale efficiency studies [6]. However, the lowering of IFT is still important; despite the current view of the interfacial solution, the injection of an alkali solution to increase the recovery efficiency of important oils, not having to optimize the solution to increase the recovery efficiency, and/or increase the efficiency of the microemulsion or developed emulsion has not been investigated to date [7–10].

The chemical mechanism responsible for IFT reduction involves forming an adsorbed film between the oil and water through the chemical interaction between the surfactant and the oil [11]. The formation of this film favors the formation of oil banks inside the reservoir, which also improves oil recovery [12].

The use of polymers in EOR processes decreases the mobility of the injected water, and consequently, increases the horizontal sweeping efficiency. The injection of polymers into oil reservoirs is successful in homogeneous formations or formations with a low degree of heterogeneity, injections with a mobility ratio between 5 and 40, absolute permeability in the least permeable region greater than 20 mD, reservoirs with maximum temperatures of 95 °C, and formations with low clay and salt content [13–15].

In summary, the addition of a polymer increases the viscosity of the displacing phase and reduces the effective permeability of water, resulting in a reduction in the mobility rate of the injected water [16]. Polymer injection is a low-cost EOR method that is widely applied and remains very promising [17].

To implement an EOR method, some preliminary criteria must be taken into account at the initial stage of an injection project. Based on certain petrophysical characteristics and properties of the fluid that one wishes to exploit, it is possible to recognize the best method of EOR for a specific reservoir [18]. Table 1 presents the main screening criteria that are taken into consideration to identify whether a reservoir is a candidate for ASP injection.

In the last 30 years, most tests using ASP injection were carried out in the Daqing, Shengli, and Karamay oil fields of China [20]. In the late 1990s, several field projects using this method were carried out in the United States. While the isolated injection of some surfactants and polymers has disadvantages, such as the excessive loss of surfactant and polymer by adsorption, the ASP injection mitigates such problems through the synergistic combination with alkali [21].

Several works regarding the full-scale application of ASP injection have been published in the last two decades [22–27]. Several authors have highlighted the need to develop more economical surfactants in weak alkaline systems and polymers that are tolerant to temperature and pH variations. In addition, the chemical constitution of fluids must be considered environmentally acceptable for use in onshore and offshore oil fields.

Currently, the Daqing oil field represents one of the most significant EOR projects using ASP injection. ASP solution injections have been studied and tested in Daqing for over 30 years. Wang et al. [28] reported the experiences of applying ASP injection in the Daqing Xingbei oil field. According to the authors, the injection of the ASP solution generated several operational problems, such as the deposition of oil aggregates, waxes, asphaltenes, degraded polymers, microorganisms, clays, sand, and adsorbed water in the pipelines and the generation of a high volume of foam, making it difficult to separate oil and water. Another reported problem is the treatment of processed water for disposal and reinjection into reservoirs. This water contains a high content of oily solids and chemicals adsorbed to oil droplets.

Certain properties are considered essential to evaluate the efficiency of ASP injection in advanced recovery processes, such as alkali, surfactant, and polymer concentration, rheology, viscoelasticity, injectivity, and surfactant and polymer adsorption.

It should be noted that compared to miscible methods and other chemical methods, the cost of an ASP injection project is generally high with values ranging from USD 6 to 11 per additional barrel, and therefore requires a more detailed technical/economic assessment regarding the candidate reservoir for the application of the technique [29,30]. The chemical substances and their quantities used in the process make ASP injection more expensive, which limits it from an economic point of view. However, there has been a recent increase in interest in the injection of the ASP solution because the price of oil has been increasing progressively to the point that the process becomes profitable.

The influence of the concentration of each compound in the ASP solution on oil recovery is of fundamental importance for the analysis of the technical/economic feasibility of the injection project [31,32]. In experiments carried out by Sharma et al. [33], the ASP solution was composed of 5000 mg L⁻¹ of NH₃ alkali, 6500 mg L⁻¹ of surfactant B, and 5500 mg L⁻¹ of AN-125 polymer. This solution achieved an oil recovery of approximately 91 % in the tertiary phase.

To evaluate the adaptability of the studied reservoir to ASP injection, Sun et al. [34], tested the Saertu, Xingshugang, and Lamadian oil fields of Daqing. Their solution consisted of 12,000 mg L⁻¹ of alkali, 3000 mg L⁻¹ of surfactant, and 2000 mg L⁻¹ of polymer. The maximum oil recovery obtained was 34.1 % in the Saertu field.

Nowrouzi et al. [35] used 2500 mg L⁻¹ of NaOH alkali, 5500 mg L⁻¹ of anionic surfactant synthesized from chicken fat residues,

and 2000 mg L⁻¹ of polymer extracted from the Hollyhocks plant in their ASP solution. This solution was responsible for recovering 27.9 % of oil in the advanced phase.

Nowrouzi et al. [36] studied the efficiency of an anionic surfactant synthesized from rapeseed oil at a concentration of 4500 mg L⁻¹. The alkali used was NaOH at a concentration of 2000 mg L⁻¹ and the concentration of the PHPA polymer was kept at 1000 mg L⁻¹. This combination achieved a 25.7 % recovered oil fraction.

More recently, Nowrouzi et al. [37] evaluated the efficiency of a natural surfactant extracted from a plant to improve oil recovery from petroleum carbonate reservoirs. The composition of the ASP solution used was 4843 mg L⁻¹ of anionic surfactant synthesized from the extract of the *Myrtus Communis* plant, 2500 mg L⁻¹ of NaOH alkali, and 1000 mg L⁻¹ of the PHPA polymer. This solution was able to recover 16.4 % of oil after the secondary phase.

From these studies, it can be observed that variations in the concentrations of the components of the ASP solution directly influence the recovered fraction of oil. Thus, in the present study, we conducted a more in-depth investigation of the influence of the quantities of each compound of the ASP solution. This should decrease the cost of ASP injection projects.

A complete factorial experimental design was performed with combinations of three variables (alkali/surfactant/polymer) and three replications of the central point (2³ + 3). For the statistical analyzes, the following independent variables were defined: alkali concentration, surfactant concentration, and polymer concentration, aiming to investigate their effects on the EOR process with the minimum of experiments to determine the recovered fraction of petroleum, which is the response variable.

2. Materials and methods

2.1. Materials

Synthetic production water was prepared using sodium chloride (NaCl, analytical standard; DQC™) and sodium sulfate (Na₂SO₄, analytical standard; DQC™). Synthetically produced water containing 40,000 mg L⁻¹ of NaCl and 13,000 mg L⁻¹ of Na₂SO₄ was placed inside the silo and injected through a high performance liquid chromatography (HPLC) pump. The ionic concentrations, density, and viscosity of the synthetic production water used for conventional oil recovery are presented in Table 2.

ASP solutions were prepared using sodium carbonate (Na₂CO₃, analytical standard; Lumatom™) as the alkali, lauryl sodium sulfate (LSS, analytical standard; Synth™) as the surfactant, and commercial xanthan gum (analytical standard; Makeni Chemicals™) as the polymer.

The addition of Na₂CO₃ alkali accelerates the neutralization of organic acids present in the oil so that the emulsified oil accumulates in the pores, forming a continuous oil bank, and generating a favorable pressure gradient along the rock sample [38–40].

Compared to other surfactants such as ammonium dodecyl sulfate, sodium laurieter sulfate, Sorbitan Monolaurate (SPAN-20), and Polysorbate-20 (TWEEN-20), LSS was very efficient in reducing IFT in high salinity environments [41–43].

Xanthan gum is one of the most widely used polymers in the petroleum industry. It exhibits characteristics that increase the efficiency of the technique, such as complete solubility in water at different temperatures, producing high viscosities (remaining unchanged in the temperature range from 0 to 100 °C) at low concentrations, and resistant to thermal degradation. This polymer is compatible with saline environments, and it is also useful as an additive in advanced petroleum recovery fluids [44–50].

2.2. Crude oil

The crude oil used in the displacement tests was provided by the Petrobras company and originated from the Carmópolis field in the state of Sergipe, Brazil. The physicochemical properties of this crude oil are summarized in Table 3.

According to Table 3, the crude oil properties are compatible with the application of EOR using an ASP solution as the injection fluid [51,52].

2.3. Sandstone rock samples

The rock samples used in the injection tests originated from the Botucatu formation. This formation is in the city of Ribeirão Claro in the state of Paraná, Brazil, and is present over a vast area in South America. The heterogeneity index of the Botucatu formation samples is comparable to those of the Berea sandstones, which are considered highly homogeneous. The rock samples used in the injection tests have an average diameter and length of 3.8 and 7.5 cm, respectively. After the sample is placed and properly confined inside the core

Table 2
Characterization of synthetic production water.

Description	Result			Standard
Total salinity (mg/L)	C _{cation}		C _{anions}	–
	Na ⁺		Cl ⁻ SO ₄ ²⁻	
53,000	863.736		126.836 99.426	
Density at 60 °C (g/mL)	1.029 ± 0.005			ASTM D-5002
Viscosity at 60 °C (cP)	0.60 ± 0.04			ASTM D-445

Table 3
Properties of crude oil originating from Carmópolis-SE, Brazil.

Property	Defined value	Standard
Pour point (°C)	20	ASTM D97
Density at 20 °C (g/mL)	0.900 ± 0.005	ASTM D-5002
Density at 60 °C (g/mL)	0.890 ± 0.005	ASTM D-5002
Viscosity at 60 °C (cP)	42.43 ± 0.03	ASTM D-445
BSW (%)	50	NBR-14647
Oil gravity (°API)	25.72	ASTM D-5002

holder, saturation of the core holder with synthetic production water is initiated.

The porosity of the core was calculated during the injection of synthetic production water using a volumetric balance. The difference between the volume of synthetic production water that entered and left is the volume that was retained in the core. Complete saturation is observed when there is no further variation between the inlet and outflow rate of the rock sample. The volume of water that was retained in the rock sample is the porous volume of this core.

After stabilizing the injection pressure in the core, the outflow of the water from the core holder was measured with the aid of a beaker and a stopwatch. The permeability of a core was calculated by considering the flow, dimensions of the rock sample, pressure, and viscosity of the fluid.

2.4. Factorial experimental design

To analyze the effect of the concentration of each constituent of the ASP solution on the oil recovery, a factorial experimental design was carried out with three replications at the central point ($2^3 + 3$). Table 4 shows the levels for the factors and the concentration of each component used in each of the 11 planned injection experiments.

The experimental values obtained for the EOR factor using the ASP solutions were analyzed through multiple regression using Statistica® version 7.0. With this statistical analysis, it was possible to verify the factors that affect the responses in a linear manner and their interactions. Multiple regression was performed using the coded independent variables to replace in a standardized way the real values of the factors so that the statistical analyzes are not negatively impacted by the diversified range that the factors could have. An analysis of variance (ANOVA) was performed to verify if the mathematical model obtained in the multiple regression is statistically significant. The confidence level adopted for the statistical analyzes was 95 %.

The regression was performed with the results of the injection tests carried out in the laboratory, and it is possible to identify a mathematical model that demonstrates how the variables influence the process and how they interact with each other. This first-order equation with interactions was used to plot a response surface. Equation (1) shows a first-order equation with standardized interactions for three independent variables.

$$\gamma = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_{12} \times 1 \times 2 + \alpha_{13} \times 1 \times 3 + \alpha_{23} \times 2 \times 3 \quad (\text{Equation 1})$$

where X_1 , X_2 , and X_3 are the planning variables, α_0 is the coefficient referring to the intersection point, α_1 , α_2 , and α_3 are the coefficients referring to linear effects, and α_{12} , α_{13} , and α_{23} are coefficients referring to the double interaction effects of the variables.

2.5. Physicochemical characterization of ASP solutions

The ASP solutions used in the tests were characterized by viscosity, IFT, density, and pH. These are the main parameters that directly influence the synergistic interactions of the ASP fluid with the porous medium.

To ensure that the solution was completely homogeneous, 20 mL was stirred at 1500 rpm for 5 h using a Quimis Q235 electronic mechanical stirrer. The solution was then transferred to ten 15-mL falcon tubes and centrifuged at 2200 rpm for 15 min to remove the

Table 4
DOE matrix for injection tests.

Experiment	Solution	Concentration of components (mg/L)		
		NaH ₂ CO ₃	LSS	Xhantam gum
1	ASP1	1200 (−1)	3000 (−1)	1000 (−1)
2	ASP2	1200 (−1)	10,000 (+1)	1000 (−1)
3	ASP3	1200 (−1)	3000 (−1)	5000 (+1)
4	ASP4	1200 (−1)	10,000 (+1)	5000 (+1)
5	ASP5	4500 (+1)	3000 (−1)	1000 (−1)
6	ASP6	4500 (+1)	10,000 (+1)	1000 (−1)
7	ASP7	4500 (+1)	3000 (−1)	5000 (+1)
8	ASP8	4500 (+1)	10,000 (+1)	5000 (+1)
9	ASP9	2850 (0)	6500 (0)	3000 (0)
10	ASP10	2850 (0)	6500 (0)	3000 (0)
11	ASP11	2850 (0)	6500 (0)	3000 (0)

bubbles incorporated by the agitation. The rheological behavior of the ASP solution was determined using a rheometer (Physica MCR 501, Anton Paar) with concentric conical geometry, following the ASTM D-445 standard at 60 °C.

The IFT measurement was performed using a tensiometer (DataPhysics® Oca 15 plus), at a temperature of 60 °C, using a thermostated accessory coupled to a thermal bath.

The density of the ASP solution was measured using a digital densimeter (DMA-5000, Anton Paar) following the ASTM D-5002 standard at 60 °C.

The pH of the solution was measured using a duly calibrated pH meter (tecnopon mPA-210) at 60 °C.

2.6. Injection tests

The experimental procedure adopted for the displacement tests was adapted from the procedure described by Ramos et al. [53].

The tests were carried out in a core holder system that was mounted inside a temperature-controlled oven at 60 °C. A preparative HPLC pump (Jasco™ PU-4087) feeds the entire system. The fluids that will be injected are stored in three aluminum silos and the injection is controlled by a system of valves. The complete experimental system is shown in Fig. 1.

The rock samples were initially immersed in synthetic saline water containing 40,000 mg L⁻¹ of NaCl and 13,000 mg L⁻¹ of Na₂SO₄ under a vacuum of 1.3 × 10⁻¹ Pa for 5 h. The pore volume of a rock sample is the difference in mass between the dry and saturated rock divided by the density of the synthetic production water. The rock sample is saturated and then confined in the core holder system under a pressure of 6.89 × 10⁶ Pa.

All fluids were injected at a constant flow rate of 1 mL min⁻¹ in the following order.

1. Two porous volumes of oil to ensure residual water saturation;
2. Synthetic saline water injection until residual oil saturation is reached;
3. ASP injection until a new residual oil saturation is reached.

To measure the recovery factor, samples produced for every 0.5 porous volume of fluid injected were collected in clean pre-weighed vials.

3. Results and discussion

3.1. Physical-chemical characterization of ASP solutions

The variations in the physicochemical properties of the ASP fluids used in the injection tests are directly related to the concentrations of the components of each fluid. The viscosity of the fluid and its IFT directly influence its mobility inside the rock, and

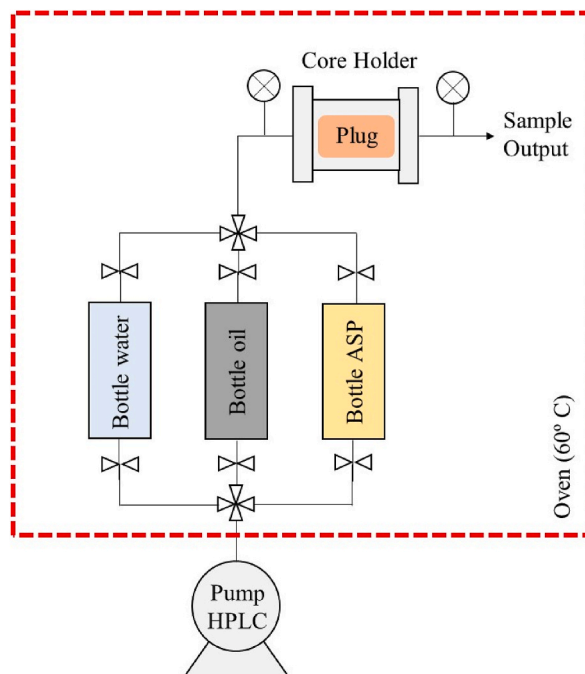


Fig. 1. Schematic of the injection test system.

consequently, the recovered fraction of oil. Table 5 summarizes the results of the physicochemical characterizations performed.

High IFT values are associated with fluids whose surfactant concentration is low, while fluids with the lowest IFT values are associated with high surfactant concentrations. The variation of the alkali concentration did not result in a significant change in the physicochemical properties of the fluid. This may be associated with the low amount of alkali added.

3.2. Injection tests

One of the factors that directly influence the physical simulation of the advanced oil recovery method is the petrophysical properties of the rock samples used in each injection test. Five rock samples with very close properties were used to facilitate the comparison between the tests and assign the recovered fraction of oil from each assay to the recovery fluid used. The procedure for cleaning the rock samples used in the injection tests was adapted from Ref. [54]. Table 6 presents the petrophysical properties of these samples.

To identify only the influence of the concentration of the compounds of the ASP solution on the recovered fraction of the oil, the same rock samples were used in the injection tests, where the concentration of surfactant and polymer remained constant, as shown by the DOE matrix for the injection tests (Table 4). Rock sample 5 underwent the cleaning procedure twice, with the objective of maintaining the same conditions in the injection tests, for the three replications at the central point, as indicated by the experimental design.

Table 7 shows the recovery factors in the conventional step with water injection (F_{RW}), the unconventional step with the injection the ASP solution (F_{RA}), and the total recovered fraction (F_R) of the injection tests. The recovery factors in water injection ranged between 30 and 36 % of the OOIP; these values are within the range reported by Ghosh et al. [55].

The injection tests that used the ASP1 and ASP5 injection fluids presented the lowest performances in the unconventional recovery stage compared to the other fluids tested. This is directly associated with the low concentrations of the independent variables because the variation of the alkali concentration did not result in a significant increase in the recovered fraction.

The ASP3 and ASP7 injection fluids achieved a higher recovery efficiency than the ASP1 and ASP5 injection fluids when the concentration of the surfactant remained constant. This is associated with the increased concentration of the polymer. The polymer promoted the reduction of the mobility of the injected water in front of the oil, culminating in an increase in the fraction recovered in the unconventional step.

For the injection test using the ASP7 fluid, there is an increase in oil recovery compared to the test using the ASP3 fluid. This may be associated with a decrease in the retention time of the polymer in the porous medium, promoted by the increase in the concentration of the added alkali.

The ASP4 and ASP8 fluids resulted in a higher recovery fraction in the unconventional step. These fluids have the highest concentrations of the surfactant and polymer. Through the synergistic behavior promoted by this association, these injected fluids behaved similar to a piston, not going beyond the oil bank that was saturating the porous medium, recovering the maximum oil. Thus, the motor force that promotes the flow of the fluid injected into the medium causes the microscopic interfaces to choose the most accessible constitutions to reach the end of the rock sample.

3.3. Experimental planning results

The statistical analysis made it possible to evaluate the effects of the variation of the concentration of the compounds in the injection fluids used in the enhanced recovery tests, as shown in Table 8.

From Table 8, the main effect of surfactant and polymer concentration were statistically significant ($p < 0.05$). In addition, the surfactant concentration is predominant for an increase or decrease in the recovered fraction.

An increase in alkali concentration (from 1200 to 4500 mg L⁻¹) increases the fraction recovered by only 1.48 %. In contrast, increasing the surfactant concentration (from 3000 to 10,000 mg L⁻¹) resulted in an 19.34 % increase in the recovered fraction.

The first-order interactions of alkali concentration with surfactant concentration, alkali concentration with polymer concentration, and surfactant concentration with polymer concentration were not statistically significant, and their effects on the recovered fraction were -0.53 %, -0.47 %, and -1.61 %, respectively. Therefore, if, for example, the alkali concentration and the surfactant

Table 5
Result of density analysis, the IFT between the ASP fluids and crude oil, pH, and apparent viscosity.

Solution	Density at 60 °C (g/mL)	pH	Interfacial tension (ASP/Crude oil) at 60 °C (mN/m)	Apparent Viscosity at 60 °C (cP)
ASP1	1.090 ± 0.005	11.00 ± 0.03	1.42 ± 0.32	0.770
ASP2	1.100 ± 0.005	11.00 ± 0.03	1.02 ± 0.40	1.490
ASP3	1.120 ± 0.005	11.00 ± 0.03	1.36 ± 0.06	2.410
ASP4	1.030 ± 0.005	11.00 ± 0.03	1.04 ± 0.38	8.700
ASP5	1.090 ± 0.005	12.00 ± 0.03	1.39 ± 0.03	0.780
ASP6	1.100 ± 0.005	12.00 ± 0.03	1.00 ± 0.42	1.500
ASP7	1.120 ± 0.005	12.00 ± 0.03	1.32 ± 0.10	2.420
ASP8	1.030 ± 0.005	12.00 ± 0.03	0.98 ± 0.44	8.720
ASP9	1.080 ± 0.005	11.00 ± 0.03	1.21 ± 0.22	4.880
ASP10	1.080 ± 0.005	11.00 ± 0.03	1.21 ± 0.,22	4.880
ASP11	1.080 ± 0.005	11.00 ± 0.03	1.21 ± 0.22	4.880

Table 6
Petrophysical properties of the rock samples used in the injection tests.

Experiment	Rock sample	Dry mass (g)	Porous volume (mL)	Porosity (%)	Permeability (mD)	Average pore diameter (μm)
1	1	135.33	21.05	24.75	383.00	3.49
5						
2	2	129.99	19.65	23.10	371.50	3.56
6						
3	3	128.35	19.60	23.04	305.50	3.23
7						
4	4	118.87	20.58	24.19	321.60	3.24
8						
9	5	140.91	20.32	23.89	358.60	3.44
10						
11						

Table 7
Recovered fraction of oil at each injection step.

Injection Fluid	F _{RW} (%)	F _{RA} (%)	F _R (%)
ASP1	32.48 ± 1.73	35.94 ± 1.67	68.42 ± 3.06
ASP 2	35.07 ± 1.73	57.30 ± 1.67	92.38 ± 3.06
ASP 3	35.48 ± 1.73	43.33 ± 1.67	78.81 ± 3.06
ASP 4	30.11 ± 1.73	61.71 ± 1.67	91.82 ± 3.06
ASP 5	30.48 ± 1.73	38.30 ± 1.67	68.78 ± 3.06
ASP 6	30.13 ± 1.73	58.83 ± 1.67	88.96 ± 3.06
ASP 7	30.47 ± 1.73	44.98 ± 1.67	75.46 ± 3.06
ASP 8	30.37 ± 1.73	62.07 ± 1.67	92.45 ± 3.06
ASP 9	32.48 ± 1.73	50.75 ± 1.67	83.23 ± 3.06
ASP 10	35.94 ± 1.73	52.97 ± 1.67	88.91 ± 3.06
ASP 11	34.37 ± 1.73	49.71 ± 1.67	84.08 ± 3.06

Table 8
Effects of independent variables on the recovered fraction of oil.

Factor	Effect	p-value	Confidence Limit	
			-95 %	+95 %
Alkali	1.47500	0.336940	-3.59130	6.54130
Surfactante	19.34000	0.003686	14.27370	24.40630
Polymer	5.43000	0.043946	0.36370	10.49630
Alkali x Surfactant	-0.53000	0.696713	-5.59630	4.53630
Alkali x Polymer	-0.47000	0.728366	-5.53630	4.53630
Surfactant x Polymer	-1.60500	0.306030	-6.67130	3.46130

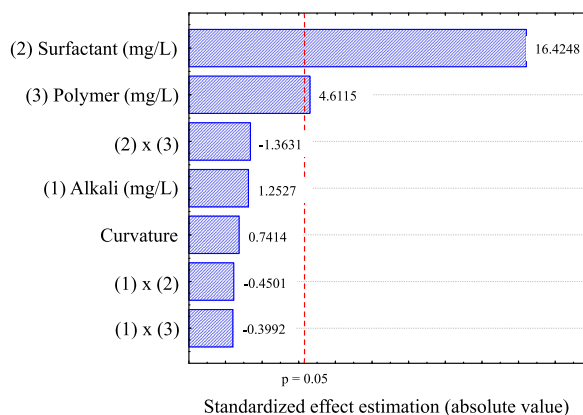


Fig. 2. Hierarchical order of the influence of factors on the EOR fraction.

concentration remain at low (1200 and 3000 mg L⁻¹, respectively) or high (4500 and 10,000 mg L⁻¹) levels, the fraction recovered will decrease by 0.53 %. Furthermore, if the surfactant and the polymer concentrations remain at low (3000 and 1000 mg L⁻¹, respectively) or high (10,000 and 5000 mg L⁻¹) levels, the recovered fraction will decrease by 1.61 %.

The p-value of the surfactant concentration is lower than 0.05, which indicates that there is a very low chance that the concentration of the surfactant will influence the value of the recovered oil fraction. Therefore, the surfactant concentration is the most significant independent variable in the experiments.

The influence of factors on the EOR fraction is presented in hierarchical order in the Pareto diagram shown in Fig. 2.

As discussed above, the surfactant and polymer concentrations are statistically significant independent variables. On the other hand, the alkali concentration and the interactions between the components that constitute the ASP fluid did not reach a p-value lower than 0.05, which indicates their weak influence on the response variable. Furthermore, the Pareto diagram shows the lack of significance of the interactions between the three parameters studied.

Equation (2) represents the mathematical model obtained in terms of the coded independent variables that were statistically significant in increasing the fraction of oil recovered. The coefficient of determination of the model indicates that 99.30 % of the variation in the alkali, surfactant, and polymer concentrations can be explained by the model.

$$F_{RA} (\%) = 50.307 + 0.737A + 9.670S + 2.71P \quad (\text{Equation 2})$$

Where F_{RA} is the recovered fraction in the enhanced stage using ASP solution (%) and A, S, and P are the coded alkali, surfactant, and polymer concentrations, respectively. According to the results presented in Table 9, the model is statistically significant because the calculated F value (62.9955) is higher than the tabulated F value (8.8867). Furthermore, the model does not suffer from a lack of fit, as the p-value of lack of fit (FA) is greater than 0.05.

The model obtained by regression has a good fit and is statistically significant. Thus, the relationship between the experimental results (recovered fraction) and the mathematical model evaluated by ANOVA is linear, as shown in Fig. 3.

The response surface methodology was used to identify an optimal region of the investigated surface, where the red region represents the surface with the highest response and the dark green region with the lowest response. From Fig. 4, it is clear that regardless of the alkali concentration (from the minimum to the maximum coded value) within the range from 1200 to 4500 mg L⁻¹, surfactant concentrations will increase or decrease the fraction of oil recovered. The recovered fraction ranged from 35.94 % when using the ASP1 fluid (low concentrations of surfactant and polymer) to 62.07 % when using the ASP8 fluid (high concentrations of surfactant and polymer).

The highest recovery fractions are obtained for surfactant concentrations in the range from 6500 to 10,000 mg L⁻¹ (from the central point to the maximum coded value); the recovered fraction did not show significant values in the surfactant concentration range from 3000 to 6500 mg L⁻¹.

The chemical nature of the surfactant used directly influences the action of capillary and gravitational forces [56–58]. For an anionic surfactant like LSS, the addition of an alkali does not significantly influence the recovery of oil; however, the scenario changes when combining a cationic surfactant with an alkali.

Other studies have compared the efficiencies of anionic and cationic surfactants in EOR, showing that anionic surfactants yields a petroleum recovery factor of 71 %, while cationic surfactants recover only 5.6 % of the original oil volume [59–62].

Li et al. [63] varied the concentrations of alkali (between 0 and 1200 mg L⁻¹ of CaCO₃), surfactant (between 0.001815 and 0.005 of the volumetric fraction), and polymer (between 0.0487 % and 0.12 %) to establish a model based on a numerical simulation of the EOR process using ASP injection. After the injection tests, they concluded that the most significant process variable was the polymer concentration and the only significant interaction occurred between the alkali and surfactant.

However, according to Madani et al. [64], there is a threshold concentration of surfactant added to the advanced recovery fluid, above which, due to thermodynamic effects, it is not possible to obtain a greater reduction of the IFT with an increase in the amount of surfactant molecules at the interface. Generally, this limit, known in the literature as critical micelle concentration, is reached when the phenomenon of micelle formation in solution starts spontaneously.

From the response surface shown in Fig. 5, regardless of the alkali concentration (from the minimum to the maximum coded value) within the range from 1200 to 4500 mg L⁻¹, the polymer concentrations influences the recovered oil fraction. The cost of a polymer injection project is high because it requires an extensive geological and engineering study [65]. The highest recovery fractions are obtained for polymer concentrations in the range from 3000 to 5000 mg L⁻¹ (from the central point to the maximum coded value). In contrast, the recovered fraction is low in the polymer concentration range from 1000 to 3000 mg L⁻¹.

Laboratory-scale evaluations using core samples and reservoir fluids must be carried out to identify a suitable polymer for the reservoir in question. In addition, a good selection can indicate mobility control, buffering trends, and adsorption losses. Significant

Table 9
Analysis of variance (ANOVA) for the influence of factors on the EOR fraction.

Information	Sum of Squares	Degree of Freedom	Mean Square	Test F	p-value
Model	819.0722	7.0000	117.0103	62.9955	0.0030
Residual	5.5723	3.0000	1.8574	–	–
FA	0.0265	1.0000	0.0265	0.0095	0.9311
EP	5.5459	2.0000	2.7729	–	–
Total	5.5459	2.0000	2.7729	–	–

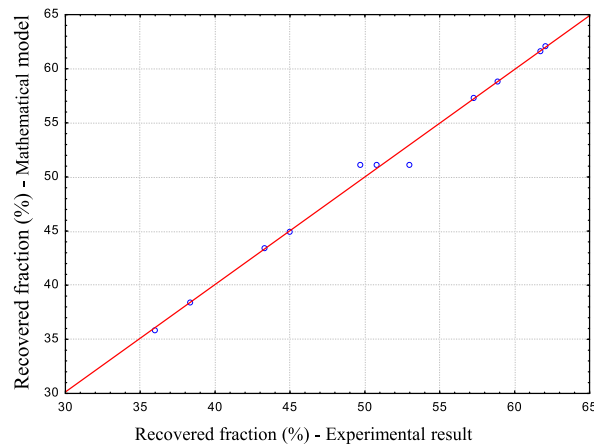


Fig. 3. Relationship between the experimental results and the mathematical model.

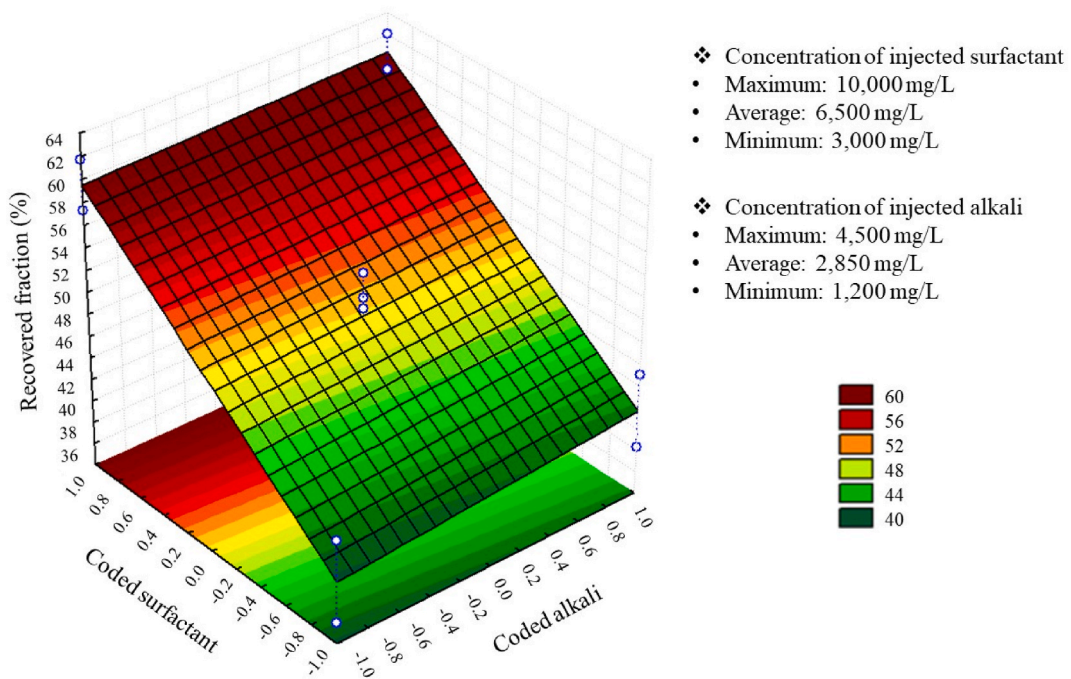


Fig. 4. Response surface of the recovered oil fraction as a function of coded surfactant and coded alkali concentrations.

interactions between the porous medium and the transported polymer molecules can occur, causing polymer retention on the porous surface. This retention can cause decreases in the efficiency of polymer injection and the permeability of the rock [66].

According to Huang et al. [67], when Na_2CO_3 alkali is dissolved in synthetic production water, Na^+ ions produce a shield in the negatively charged polymer molecules. In addition, the repulsion between the carboxyl groups in the molecular chain is weakened and the polymer chain undergoes contraction. This strong electrostatic repulsion weakens the adsorption of LSS molecules on the surface of polymer macromolecules. In this case, the effect of sulfonate on the polymer molecule is similar to that of organic salts, resulting in contraction of the 'molecular chain of the polymer.

This double compression of Na_2CO_3 and LSS on the morphology of molecular chain of the polymer decreases the susceptibility of the micromolecular aggregates in the ASP system to an adsorption process [68].

The response surface presented in Fig. 6 shows the relationship between surfactant and polymer concentrations with the recovered oil fraction. The surfactant concentration is the most statistically relevant independent variable. Low recovered oil fractions are obtained for polymer concentrations ranging from the minimum to the maximum coded value, compared to variations of surfactant concentrations.

According to Ko et al. [69], the viscosification of the aqueous phase through the addition of the polymer effectively contributes to

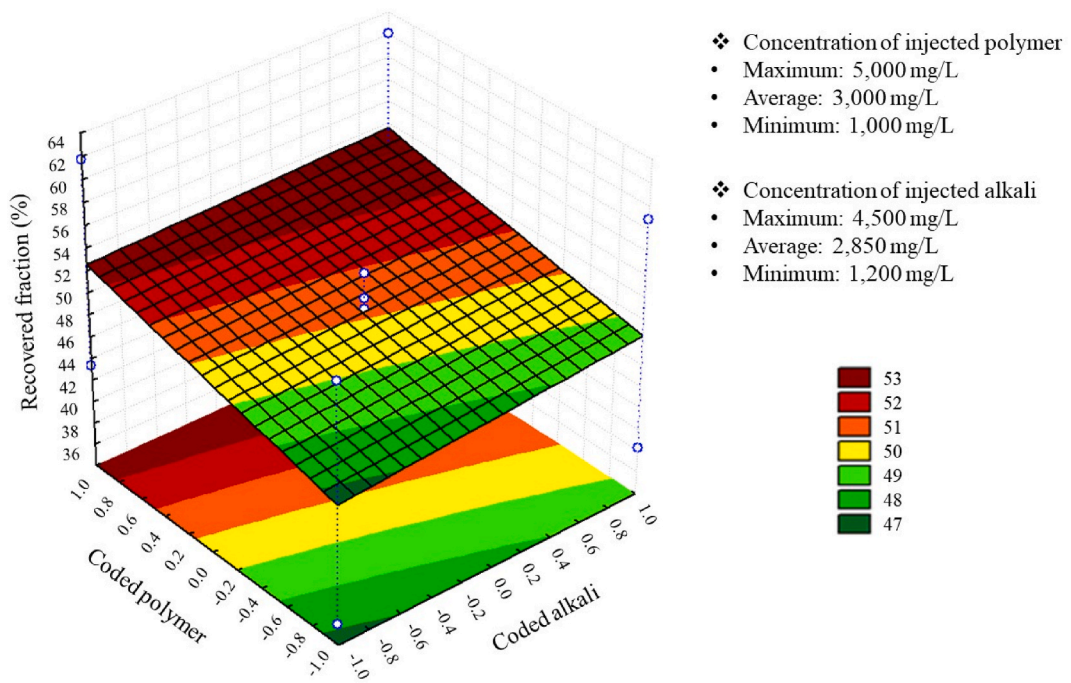


Fig. 5. Response surface of the recovered oil fraction as a function of coded polymer and coded alkali concentration.

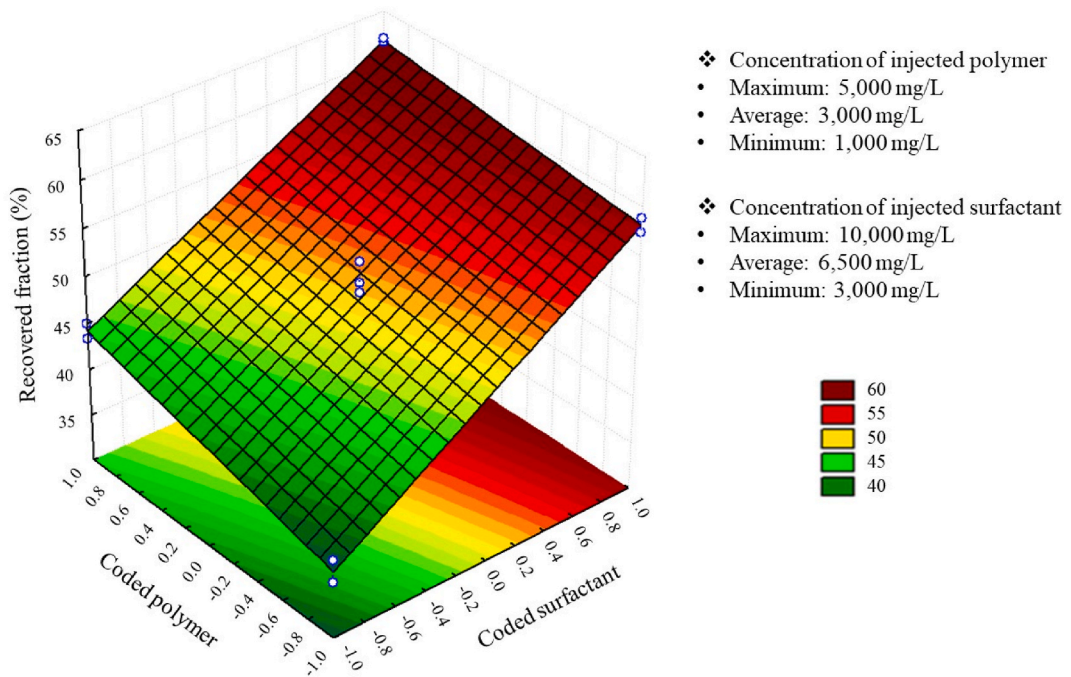


Fig. 6. Response surface of the recovered oil fraction as a function of the coded polymer and coded surfactant concentrations.

the improved EOR, and the presence of an associated surfactant can more effectively contribute to the success of the operation. In most of the studies reported in the literature, the joint injection of solutions containing surfactants and polymers is performed in banks (bank injection) to maintain mobility control. Generally, the concentration of the polymeric solution varies between 1000 and 5000 mg L⁻¹, with polyacrylamide and xanthan gum being used most often [70].

4. Conclusions

- The use of factorial planning in the present study explained the most significant variables of the EOR process and showed that the first-order interactions were not statistically significant;
- Fluids with low surfactant and polymer concentrations resulted in lower oil recoveries in the advanced stage;
- An increase in alkali concentration to 4500 mg L⁻¹ raised oil recovery to 2.36 %. This increase can be considered to be low; however, this full-scale gain can be attractive for a project aimed at implementing an improvement technique;
- Fluids with high surfactant and polymer concentrations resulted in a higher recovery fraction in the unconventional step;
- The p-value of the surfactant concentration is less than 0.05, which indicates that there is a very low chance that the concentration of the surfactant will influence the value of the recovered oil fraction. This makes surfactant concentration the most significant independent variable in all assays.
- In fluids where the polymer concentration is at a maximum, the apparent viscosity is higher than that of other fluids. This indicates that the salinity of the synthetic production water did not contribute to the chemical degradation of the commercial xanthan gum used in the formulation of ASP fluids;
- The experimental design presented in this work provides guidelines for future injection projects regarding the maximum and minimum concentrations of alkali/surfactant/polymer to obtain high recovered fractions of petroleum.

Data availability statement

Data included in article/supp. material/referenced in article.

Additional information

No additional information is available for this paper.
INTERNA.

CRedit authorship contribution statement

Landson Soares Marques: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **Pamela Dias Rodrigues:** Writing – review & editing, Validation, Methodology, Data curation, Conceptualization. **George Simonelli:** Validation, Supervision, Formal analysis, Data curation, Conceptualization. **Denilson de Jesus Assis:** Visualization, Validation, Funding acquisition, Formal analysis. **Cristina M. Quintella:** Visualization, Validation, Supervision. **Ana Katerine de Carvalho Lima Lobato:** Visualization, Validation, Supervision, Conceptualization. **Olívia Maria Cordeiro de Oliveira:** Visualization, Validation, Supervision, Conceptualization. **Luiz Carlos Lobato dos Santos:** Writing – review & editing, Writing – original draft, Validation, Supervision, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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