



Effect of polyamide on reservoir rocks in crude oil fields

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ABSTRACT: The use of polymers to increase the recovery factor of crude oil from depleted deposits is mainly due to the property of the polymer solution to show in the porous medium resistance, which added to the effect of increasing the viscosity of the solvent (field water) and leads to an increase in flooding efficiency. The explanation lies in the reduced reactivity of the reservoir rocks with the solvent treated with the polymer solution, which increases the pore space's flow and flooding. In this article, we have analyzed the behavior of partially hydrolyzed polyacrylamide, the most commonly used polymer at the moment, in contact with reservoir rocks in oil fields undergoing tertiary recovery processes..

KEYWORDS: Partially hydrolyzed polyamide, Simulation equations, Numerical modeling, Oil fields, Tertiary oil recovery

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I. INTRODUCTION

Hydrolyzed polyacrylamide is a polymer consisting of long chains of carbon atoms (linear structure) to which sodium carboxyl groups and amines are alternately attached.

These molecules have a molecular weight of 10^6 and are 1 micron in size (at a carboxyl/amide ratio of 0.25).

Polyacrylamide is derived through a meticulous process of polymerizing acrylamide, followed by partial hydrolysis of the homopolymer with dilute sodium hydroxide, ensuring the purity and quality of the product.

It should be noted that in the case of partially hydrolyzed polyacrylamide, the formed molecule is wrapped in a spherical shape.

When the polymer dissolves in fresh water, the carboxyl groups along the chain ionize, and the resulting negative charges repel each other. This causes the polymer to unfold and expand and a sharp increase in water viscosity.

By using salt water (increasing the concentration of NaCl) in the mixture with the polyacrylamide solution, the viscosity of the solution will decrease (resulting in electrostatic shielding of the polymer chain).

II. METHODS AND EXPERIMENTS

In the first experiment, we studied the experimental behavior of the apparent relative viscosity (which is the ratio between the viscosity of the polymer and the viscosity of the solvent) as a function of the shear rate (for different values of the salt concentration in the aquifer from the studied crude oil deposits) (Table 1).

The equations of variation of the shear rate as a function of viscosity (at a specific salinity of the reservoir water) are given in Table 2.

Our observations revealed that the mathematically established predictions hold true in practical scenarios. This means that the behavior of the polymer in various salinities of the reservoir water can be accurately predicted, a significant finding with potential real-world applications.

It is understandable that hydrolyzed polyacrylamide behaves in a saline water solution with a over 3% salt concentration.

The viscosity value changes very little, and in the presence of (bivalent) calcium ions, the polymer solution has an increased viscosity, thus affecting its efficiency.

Table 1. Experimental behavior of apparent relative viscosity (which is the ratio of polymer viscosity to solvent viscosity) as a function of shear rate (for different values of salt concentration in the aquifer of the crude oil fields studied).

| The salinity of the water (of the solvent), % | Shear rate (s ⁻¹)/apparent viscosity (polymer viscosity/solvent viscosity) | | | | | | |
|---|--|------|------|-----|------|------|------|
| | 50 | 100 | 200 | 500 | 1000 | 2000 | 5000 |
| 0 | 22 | 15,9 | 13,1 | 7,9 | 5,8 | 4,3 | 3,9 |
| 0,001 | 11,1 | 10,4 | 11,9 | 6,8 | 5,1 | 4,1 | 3,8 |
| 0,01 | 6,9 | 5,8 | 4,9 | 4,3 | 4,1 | 3,5 | 3,2 |
| 0,1 | 4,1 | 3,9 | 3,7 | 3,4 | 3,3 | 3,0 | 2,8 |
| 0,5 | 3,0 | 2,9 | 2,7 | 2,6 | 2,5 | 2,4 | 2,3 |
| 3 | 1,9 | 1,8 | 1,7 | 1,6 | 1,5 | 1,4 | 1,3 |
| 10 | 1,7 | 1,6 | 1,5 | 1,4 | 1,3 | 1,2 | 1,1 |

Table 2. Variation equations of the shear rate as a function of viscosity (at a certain salinity of the reservoir water)

| The salinity of the water (of the solvent), % | The prediction equation (y is the apparent viscosity (polymer viscosity/solvent viscosity) and x is the shear rate (s ⁻¹)) | R ² |
|---|--|-------------------------|
| 0 | $y = -3,94\ln(x) + 34,647$ | R ² = 0,9129 |
| 0,001 | $y = -1,777\ln(x) + 18,185$ | R ² = 0,9545 |
| 0,01 | $y = -0,73\ln(x) + 9,2217$ | R ² = 0,9221 |
| 0,1 | $y = -0,285\ln(x) + 5,2083$ | R ² = 0,9946 |
| 0,5 | $y = -0,154\ln(x) + 3,5733$ | R ² = 0,9817 |
| 3 | $y = -0,131\ln(x) + 2,4029$ | R ² = 0,9984 |
| 10 | $y = -0,131\ln(x) + 2,2029$ | R ² = 0,9984 |

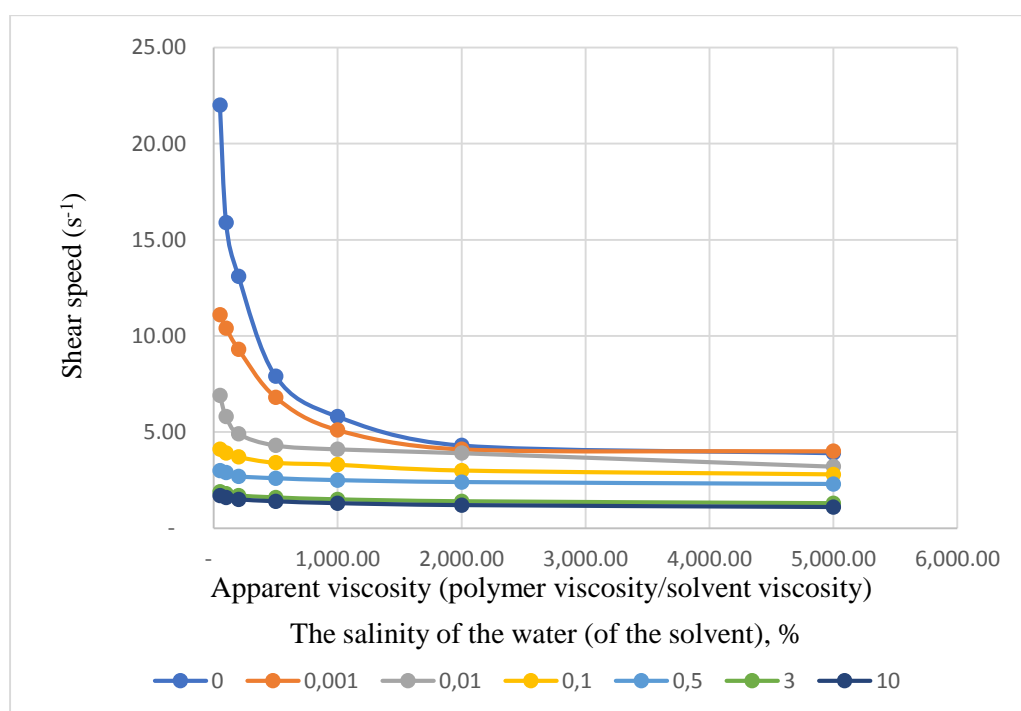


Figure 1. Variation of shear rate as a function of apparent viscosity at various concentrations of salt in the waters used

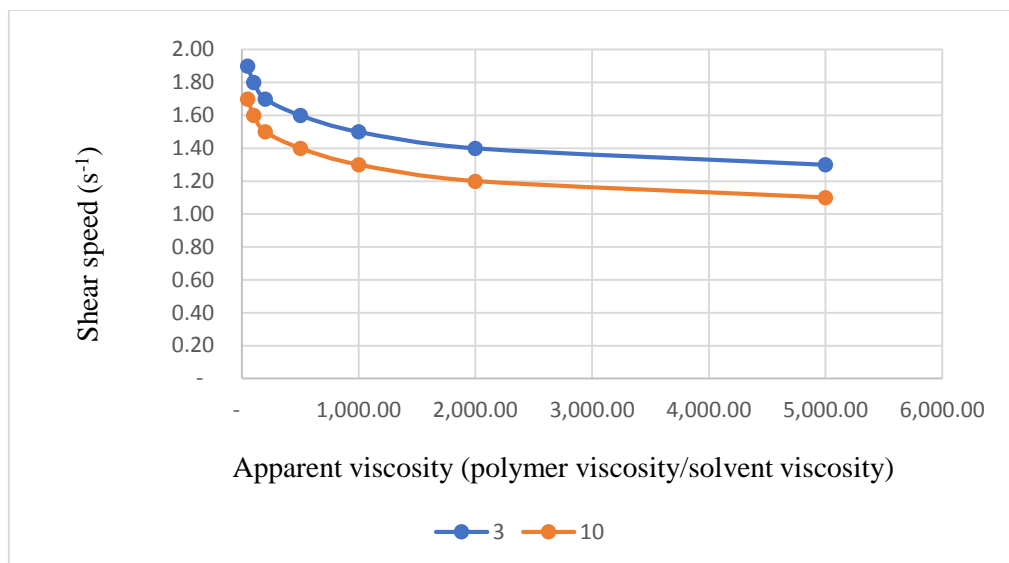


Figure 2. Variation of shear rate as a function of apparent viscosity at various concentrations of saline water (active deposit aquifer)

Another laboratory analysis allowed us to establish the mobility of the partially hydrolyzed polyacrylamide solution by determining the viscosity of the saline polymer solution when passing through a porous medium and an Engler viscometer (Table 3) [1,2,3,4,5].

Table 3. Values of the viscosity of the polymer solution of various concentrations, when passing through a porous medium of constant permeability.

| Concentrația de polimer în apa sărată (%) | Vâscozitatea determinată cu aparatul Engler, cP | Vâscozitatea determinată la trecerea prin mediul poros (cu ajutorul relație lui Darcy), cP |
|---|---|--|
| 0 | 0 | 0 |
| 1 | 2,3 | 21,1 |
| 2 | 4,9 | 35,6 |
| 3 | 8,8 | 50,1 |
| 4 | 18,8 | 69,7 |
| 5 | 27,3 | 89,9 |

In this case, we established two polynomial equations for the variation of viscosity (y) with polymer concentration (x) in 3% saline water (reservoir water).

The equation takes the following form for the viscosity of water with a specific type of partially hydrolyzed polymer, polyacrylamide.

$$y = -0,0675x^5 + 0,6125x^4 - 0,8875x^3 - 3,9125x^2 + 25,355x - 6E-09 \quad (1)$$

And for the polyacrylamide viscosity (y) traversing a volume of about 1 m length and 10 cm diameter filled with sand (with a permeability of 10^{-1} Darcy) the equation is of the form (x is polymer concentration (x) in a 3% saline water (reservoir water)):

$$y = -0,135x^5 + 1,5083x^4 - 5,5083x^3 + 8,1417x^2 - 1,7067x - 2E-0 \quad (2)$$

As can be seen in graph 2, the variation of the viscosity of the polymer solution calculated on the basis of Darcy's relation will be 5-20 times higher than that determined in the laboratory, in the concentration range of 0.025 and 0.20%, if the environment is considered perfectly homogeneous and constant porosity (effective permeability).

In reality, the following is observed:

- The effective permeability of the porous medium is not constant,
- The effective permeability of the porous medium decreases due primarily to the resistance to the flow,
- We cannot define a uniform relationship for all types of porous media that ensures a constant viscosity variation (or mobility of the polymer solution) as a function of permeability k^p .

In practical applications, we use a residual resistance factor to determine the permeability reduction of the porous medium or the reduction in the mobility of the unadded polymer water that is injected after the polymer solution (compared to the initial water flow).

This factor, as referenced in [1,2,3,4,5], is a key tool in our understanding and management of fluid dynamics in polymer solutions.

$$R_r = \frac{\lambda_a}{\lambda_{a \text{ after polymer}}} \quad (3)$$

At the same time, we also use in practice a factor for determining the coefficient of reduction of the mobility of the polymer solution compared to the water with which the polymer solution was prepared:

$$R = \frac{\lambda_a}{\lambda_{polymer}} \quad (4)$$

Where:

- λ_a is the mobility of water at saturation,
- $\lambda_{a \text{ after polymer}}$ is the mobility of water at saturation after polymer,
- $\lambda_{polymer}$ is the mobility of the polymer.

In table 4 we analyzed the variation of the reservoir rock resistance factor as a function of a cumulative volume $\frac{V_{inj}}{V_{pores}}$ of polymer solution passed through a core.

The salt concentration of the water used in washing the core was 3%, and after the passage of about 100 pore volumes, a resistance factor value of about 9-10 is reached.

So we can say that in this case the polymer solution will not completely fill all the pores, but will also ensure the replacement of the crude oil in the reservoir.

In figure 3 I have reproduced the way the polymer behaves on the rock surface, being a paradox the attraction of polymer particles by adsorption to the rock surface (and thus to the filling of free pores).

In graph 4, we have reproduced the behavior of the cumulative volume and therefore of the flow resistance factor of the polymer

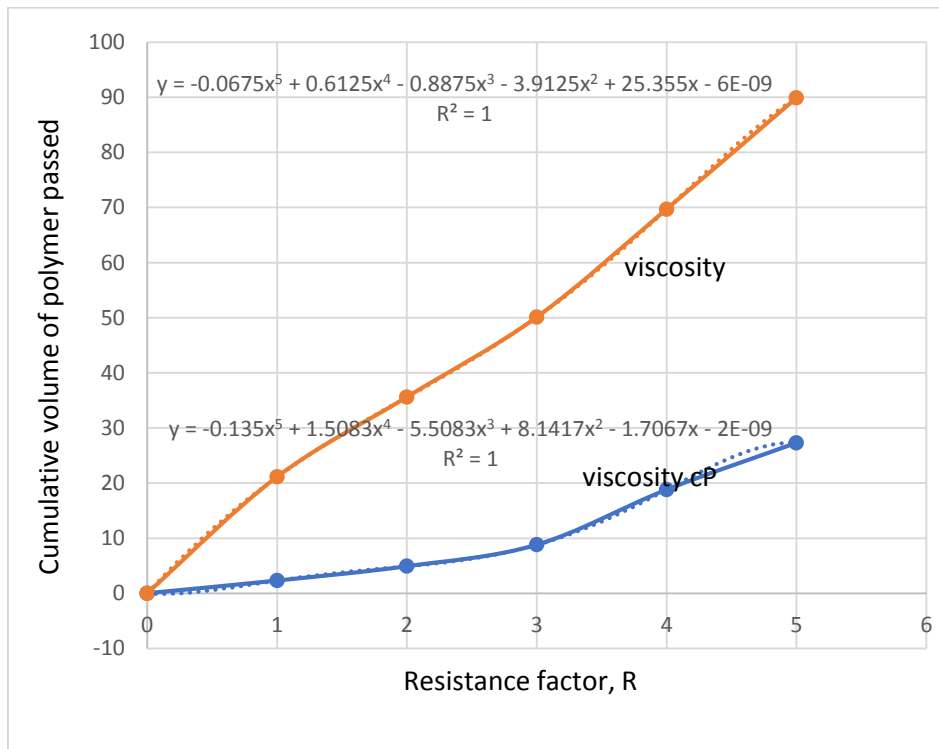


Figure 3. Variation of the viscosity of the polymer solution of various concentrations, when passing through a porous medium of constant permeability

Table 4: Resistance factor values depending on the cumulative volume of polymer passed through a core, $\frac{V_{inj}}{V_{pori}}$

| Resistance factor, R | Cumulative volume of polymer passed through a core, $\frac{V_{inj}}{V_{pori}}$ |
|----------------------|--|
| 1 | 0 |
| 6 | 10 |
| 8 | 20 |
| 8,1 | 30 |
| 8,2 | 40 |
| 8,3 | 50 |
| 8,4 | 60 |
| 8,5 | 70 |
| 8,6 | 80 |
| 8,7 | 90 |
| 8,8 | 100 |
| 8,9 | 110 |

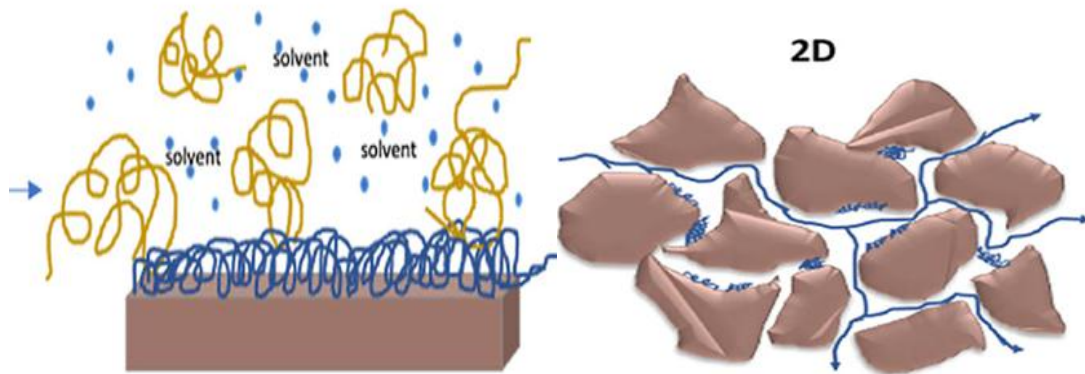


Figure4. Adsorption of polymer to the surface of rocks (processed scheme) [1,2,3,4,5]

The adsorption on the surface of the rocks, thus determined the reduction of the mobility of the polymer and at the same time the modification of the gel structure by the modification (crossing) of the polymer (of the polymer chains) which will lead to clogging (blocking of the pores) and increasing the possibility of fluid flow .

In the laboratory we determined the adsorption on silicon, for a polyacrylamide solution of 0.05% concentration partially hydrolyzed in water, it increases from the value of 0.01 mg/m² to 0.05 mg/m² when the concentration in NaCl increases from 0.5% to 10%.

It is observed that the adsorption increases for pH values lower than value lower to 7.

Thus we can conclude that the polymer will behave as a fixed polymer structure (adsorbed to the rock surface) and a mobile fraction due to the presence of deformed polymer molecules in the flow pore area.

Thus, it can be stated that for a porous medium of sand with a permeability of 140 mD, replacing saline water with 20 g/l NaCl, we observed a presence of the polymer with a concentration of 400 ppm in the effluent, this value being approximately stabilized after 5 volumes of injected pores.

We can write a behavior equation of the form:

$$y = 3,1452x^6 - 56,293x^5 + 383,83x^4 - 1224,4x^3 + 1744,4x^2 - 657,51x - 3,2752 \quad (5)$$

$$R^2 = 0,8033$$

Where x is the volume of solution injected onto a 140 mD sand and 20 g/l NaCl saline (400 ppm polymer pusher solution) and y is the effluent concentration values in polymer (ppm).

In graph 5, I represented this behavior which thus confirms what I stated previously, namely that after the polymer is adsorbed on the surface of the rock, we will have a flow of the polymer through the sand which will have a stabilized concentration at a value of 98% of the initial value of the concentration (which confirms to us that in the first part the adsorption of the polymer takes place and then the normal flow of the polymer takes place).

On a sandstone, the experiments of injecting a polymer solution with 2% NaCl solution and 0.05% hydrolyzed polyacrylamide show us a reduction in mobility depending on the injected pore volumes and a variation in the effluent concentration (table 5).

Table 5. Effluent concentration values in polymer (ppm) as a function of solution volume injected on a 140 mD sand and 20 g/l NaCl saline water (410 ppm polymer pusher solution)

| Nr. Crt. | Solution volume injected into a 140 mD sand and 20 g/l NaCl saline water (400 ppm polymer pusher solution) | Effluent concentration values in polymer (ppm) |
|----------|--|--|
| 1 | 0 | 0 |
| 2 | 0,9 | 0 |
| 3 | 1 | 350 |
| 4 | 1,5 | 360 |
| 5 | 2 | 370 |
| 6 | 2,5 | 380 |
| 7 | 3 | 390 |
| 8 | 3,5 | 395 |
| 9 | 4 | 400 |
| 10 | 4,5 | 405 |
| 11 | 5 | 405 |
| 12 | 5,5 | 405 |

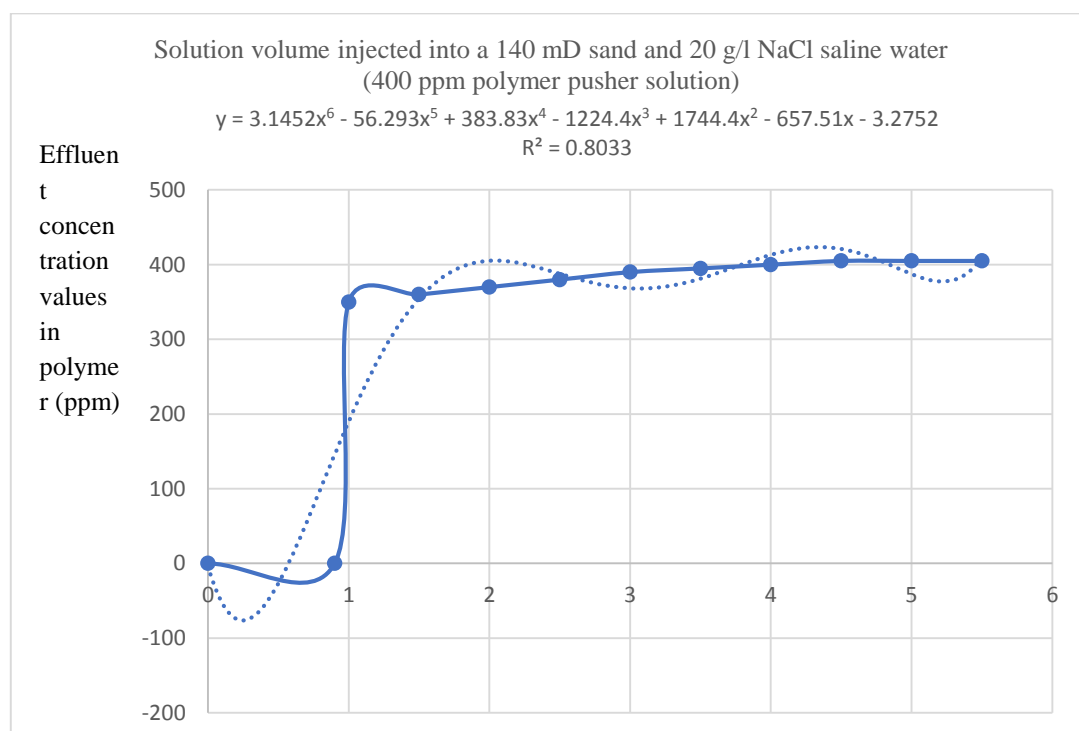


Figure 5. Effluent concentration values in polymer (ppm) as a function of the volume of injected solution on a sand with 140 mD and with saline water of 20 g/l NaCl (410 ppm polymer pusher solution)

Table 6. The values of effluent concentration in polyacrylamide, %, depending on the injection pressure, atm, on the injected pore volumes and on the concentration of the effluent in polyacrylamide, %.

| Injected pore volumes | Injection pressure, atm | Mobility reduction, cP | effluent concentration in polyacrylamide, % |
|-----------------------|-------------------------|------------------------|---|
| 14 | 0,05 | 3,1 | 0,01 |
| 16 | 0,05 | 4,0 | 0,02 |

| | | | |
|----|------|-----|------|
| 18 | 0,05 | 4,1 | 0,03 |
| 20 | 1,5 | 4,2 | 0,04 |
| 22 | 1,5 | 4,3 | 0,04 |
| 24 | 2,5 | 4,4 | 0,05 |
| 26 | 2,5 | 4,5 | 0,05 |

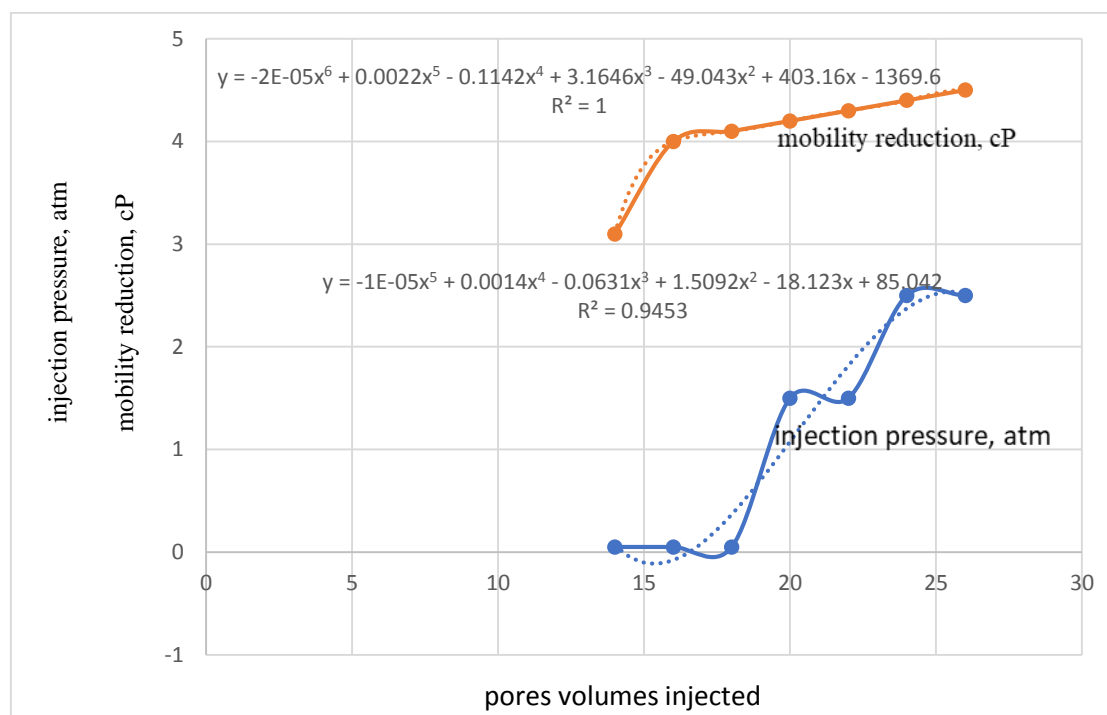


Figure 7. Mobility reduction and injection pressure depending on injected pore volumes

From the analysis of the experiment represented in graphs 6 and 7 we can conclude the following behavior of the polymer (partially hydrolyzed polyacrylamide):

a. The equations describing the mobility reduction and the injection pressure as a function of the injected pore volumes are as follows:

$$y = -2E-05x^6 + 0,0022x^5 - 0,1142x^4 + 3,1646x^3 - 49,043x^2 + 403,16x - 1369,6$$

$$z = -1E-05x^5 + 0,0014x^4 - 0,0631x^3 + 1,5092x^2 - 18,123x + 85,042$$

where:

- x represents the injected pore volumes,

- y is mobility reduction

- z is the injection pressure.

b. The equations describing the effluent concentration in polyacrylamide, % and the injection pressure as a function of the injected pore volumes, are as follows:

$$-a = -2E-06x^6 + 0.0003x^5 - 0.0138x^4 + 0.3564x^3 - 5.1272x^2 + 38.97x - 122.28,$$

$$z = -0.0004x^6 + 0.0508x^5 - 2.5154x^4 + 65.86x^3 - 960.83x^2 + 7403.5x - 23535$$

where:

- x represents the injected pore volumes,

- a represents the concentration of the effluent in polyacrylamide, %

- z is the injection pressure, atm.

c. The reduction in mobility is greater in the first part of the flow through the pores of the rocks when they are filled with polymer and thus adsorption on the surface of the rocks, and then it decreases (the graph flattens),

d. The polymer in the effluent increases according to the volume of fluid injected,

e. The need to increase the pressure to maintain a constant flow rate is also noted.

In conclusion, we can say that when the polymer flows through the rock, it is found that there is an agglomeration of the polymer molecules in the pores of the rocks, the adsorption on the structural surface of the rocks being thus also a possibility of increasing the flow speed by lubricating the flow channels.

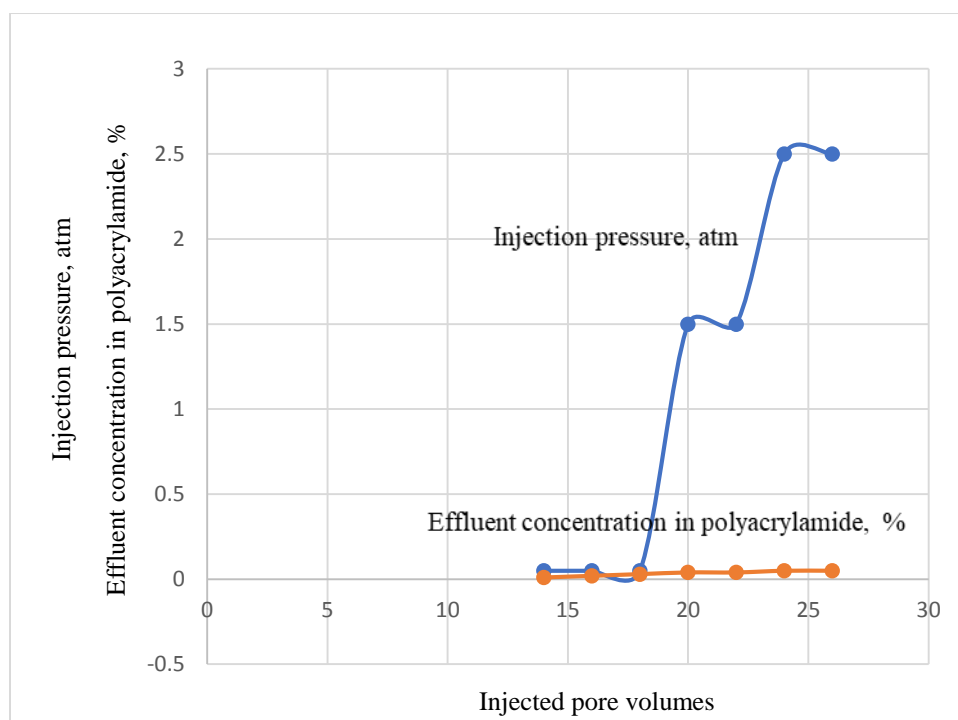


Figure 8. Effluent concentration in polyacrylamide, % and injection pressure as a function of injected pore volumes

Moreover, in an experiment carried out in the laboratory regarding the effect of polymers on the final refining products, we analyzed two polymers created in order to reduce the effect of viscosity and freezing on the mobility of petroleum fluids.

The additive made in the laboratory of the University of Oil and Gas consists of:

- 80 ml o,m,p-xylene with C_8H_{10} content 90%, Fe 0.00002 g, HCl 0.0003 acidity, evaporation resistance 0.002%, water 0.02, density 0.865

- 16 ml of liquid vinyl acetate $C_4H_6O_2$, density 0.93, boiling point $73^\circ C$,

- 4 ml of formic acid, for the elimination of biological pods,

The second additive consists of:

- 80 ml of probe condensate, density 0.705,

- 10 ml of liquid vinyl acetate $C_4H_6O_2$, density 0.95, boiling point $70^\circ C$,

- 10 ml of formic acid, for the elimination of biological poulitices,

Each additive was boiled at a temperature of 88 degrees C for 1.5 hours and then cooled.

From the analysis of the effects of the two polymers on crude oil, we found the following:

1. the freezing temperature decreases from $31^\circ C$ to $15^\circ C$, by $16^\circ C$, using additive 1 as a depressant, and decreases by $12^\circ C$, i.e. from $31^\circ C$ to $19^\circ C$, using additive 2 as a depressant ;

2. the reactivity of these additives is not lost over time (their stability was checked even after 64 hours.

I also studied under a microscope the contact between polymer (additive) and oil on a scale of 10 mm x

50.

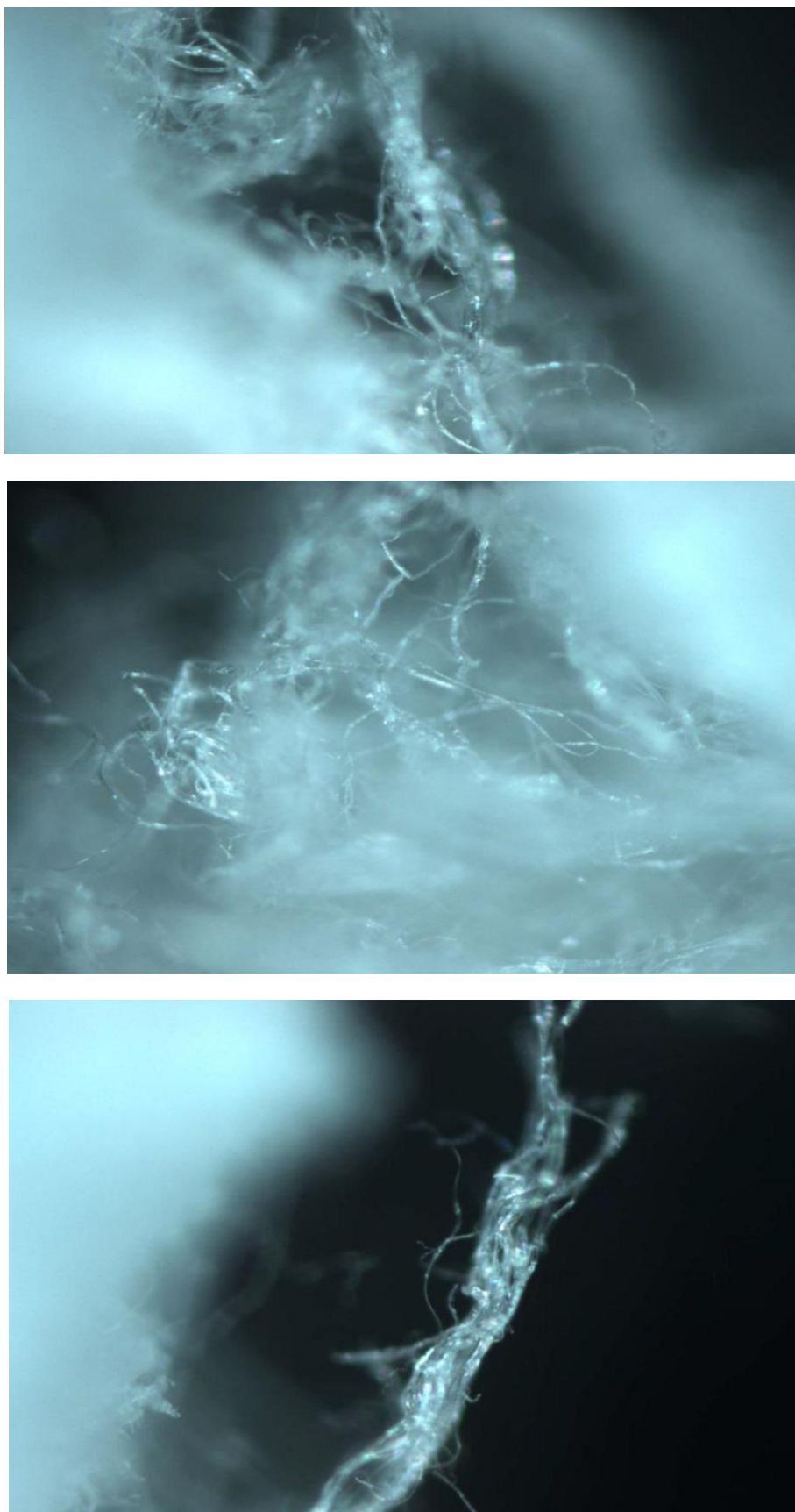


Figure 9. Reactivity of polyacrylamide with water and crude oil of density 0.850[1,2,3,4,5]

III. CONCLUSION

The three additives were also tested for their adsorption to the rock surface and pores.

In the table below we have analyzed the effect of the concentration of three polymers, namely:

a. partially hydrolyzed polyacrylamide,

b. additive 1 UPG,

c. additive 2 UPG

on their adsorption capacity on a silicate rock (on a sand with 140 mD permeability).

Table 6. Values of the adsorption capacity of the polymer, mg/m² depending on the concentration of the polymer used as a displacement support

| The adsorption capacity of the polymer, mg/m ² | Polyacrylamide polymer concentration, ppm | Polyacrylamide polymer 1 concentration, ppm | Polyacrylamide polymer 2 concentration, ppm |
|---|---|---|---|
| 0,025 | 1 | 5 | 25 |
| 0,05 | 8 | 13 | 50 |
| 0,1 | 48 | 50 | 100 |
| 0,15 | 75 | 90 | 150 |
| 0,2 | 125 | 200 | 250 |
| 0,25 | 175 | 225 | 350 |
| 0,3 | 300 | 350 | 400 |

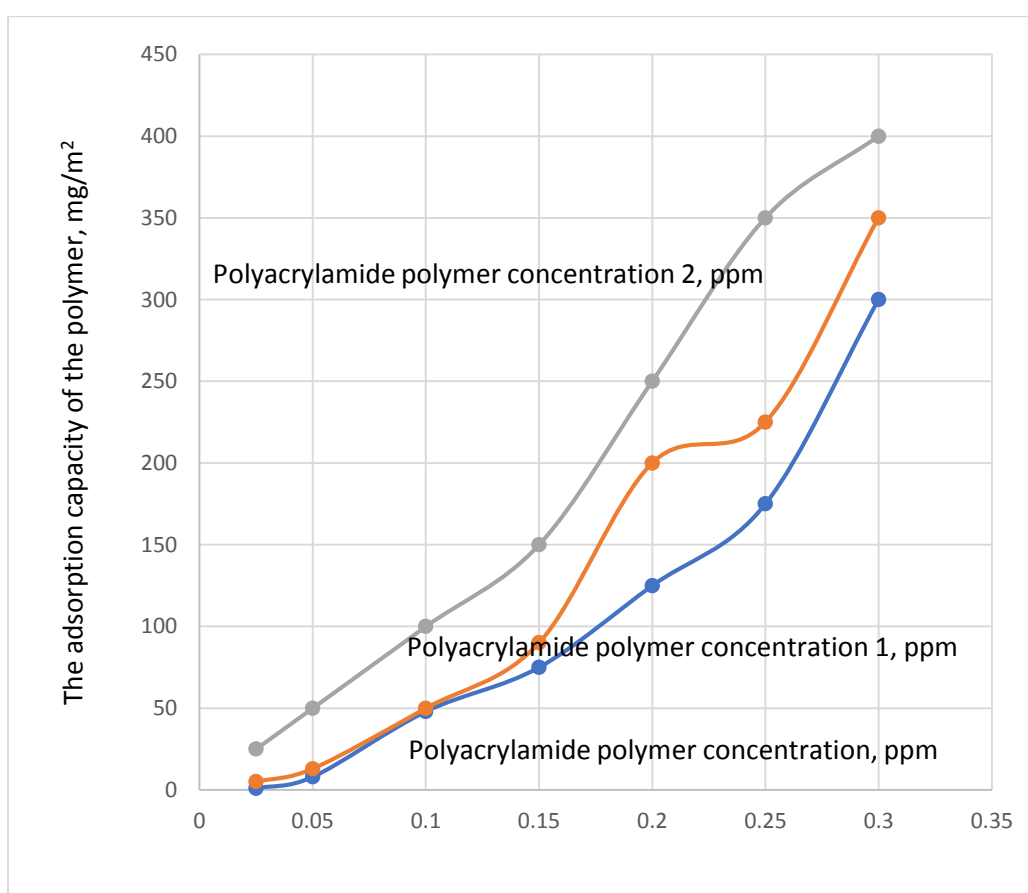


Figure 10. Evolution of the adsorption surface depending on the concentration of the polymer used for wetting

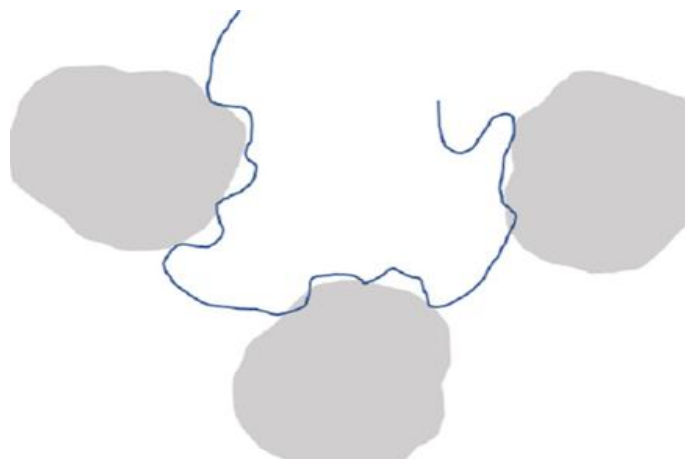


Figure 11 Adsorption of polyamides to the rocks [1,2,3,4,5,6]

We observe the following aspects regarding the wetting of the sand with the three polymer solutions treated with 5% Na Cl salt water.

If we analyze the wetted surface according to the amount of polymer, we observe the following:

a. the partially hydrolyzed polyacrylamide solution is more difficult to adsorb compared to the polymer solutions created in this work,

b. at a given moment the adsorption surface has a more flattened growth compared to the amount of polymer existing in the aqueous solution,

c. polymer 2 has the fastest adsorption capacity (so it is more useful in filling the pores of the reservoir rock and creating a mobile substrate),

d. the equations for simulating the flow through the rock (of polymer adsorption to the rock surface) depending on the amount of polymer in the aqueous solution are:

- for partially hydrolyzed polyacrylamide (y represents the adsorption capacity of the polymer, mg/m² and x is the polyacrylamide polymer concentration, ppm):

$$y = -5E-13x^5 + 3E-10x^4 - 5E-08x^3 + 4E-07x^2 + 0,0017x + 0,0286 \quad (R^2=0,9973),$$

- for polymer 1 (z represents the adsorption capacity of polymer 1, mg/m² and x is the polyacrylamide polymer concentration, ppm):

$$z = 8E-09x^3 - 6E-06x^2 + 0,0018x + 0,0217 \quad R^2 = 0,987$$

- for polymer 2 (v represents the adsorption capacity of polymer 2, mg/m² and x is the polyacrylamide polymer concentration, ppm):

$$v = 8E-09x^3 - 6E-06x^2 + 0,0018x + 0,0217 \quad R^2 = 0,987$$

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