

Article

# Laboratory Testing of Novel Polyfraction Nanoemulsion for EOR Processes in Carbonate Formations

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**Abstract:** Nanoemulsions and polymers are widely used for increasing the efficiency of enhanced oil recovery (EOR) processes. The application of both these additives enables the synergistic use of several physical phenomena that are crucial to the process. One of the methods used for assessing these processes is laboratory core flooding tests using natural cores. In various experiments, carbonate rocks are subjected to oil displacement under high pressure and temperature. Polymer solutions and a newly developed polyfraction nanoemulsion are tested. The test results confirm the usefulness of these products for EOR processes and demonstrate their stability under high pressure, high temperature, and in the presence of H<sub>2</sub>S. Under these conditions the polymers maintain high efficiency in displacing crude oil from carbonate rocks, while the tested nanoemulsion improves the wettability of carbonate rocks and reduces interfacial tension, factors which increase the efficiency of oil displacement. The best result in the laboratory EOR simulation was obtained for polymer and nanoemulsion concentrations in dilute reservoir water of 0.05% and 1%, respectively. In this case, the measured oil recovery was 37.5% higher than that obtained when using water without additives.

**Keywords:** polyfraction nanoemulsion; chemical EOR; core floods; carbonates; contact angle

## 1. Introduction

Many oil resources are yet to be extracted from deposits that have been heavily or partially depleted. In many such deposits, primary or both primary and second enhanced oil recovery (EOR) methods have been used. Large deposits are especially interesting, from the point of view of the application of EOR methods [1–3]. Various classifications of enhanced oil recovery methods and conditions for their use have been provided in the literature, defined for very heavy, heavy, and other hydrocarbons [2,4–6]. In the former group, EOR methods such as the injection of water, chemical materials, gas, heat, as well as other methods such as microbiological, ultrasonic, and so on have been distinguished. The next classification criterion may be the type of deposit rock. In this case, production support methods (i.e., EOR) have been distinguished for sandstone and carbonate deposits [6–12].

Regardless of the adopted classification and division of secondary methods to support oil production, each case should be considered individually. Many examples can be found in the literature from laboratory tests through to computer simulations and test pilots, ending with the analysis of completed projects in specific fields [13–19]. The full cycle of preparation and implementation of an EOR project, from laboratory research to its implementation in an oil field and confirming its effectiveness, is typically complex, long-lasting and, thus, expensive. The economic situation in the oil industry, as in many others, is volatile

as the price of oil fluctuates significantly [20]. Therefore, the profitability of these projects is difficult to estimate in the long-term. However, certain assumptions and goals remain unchanged. First, one goal is striving for the efficient use of natural resources (including crude oil), where the exploitation of deposits should lead to the highest depletion factor. The efficiency of new technological processes in enhancing recovery, as well as their economic viability, are also key goals. Nanotechnology has provided huge technological breakthroughs in many areas, being considered revolutionary in many applications. The entry of engineering into the nanoscale has opened up many new areas previously inaccessible without the use of nanotechnology, as well as the possibility of modifying existing technological solutions (e.g., EOR processes). Examples of research projects or nanotechnology-based solutions have been cited repeatedly [8,14,16,20–26]. These studies have shown that during EOR processes, rock wettability is particularly important in carbonate rocks. The authors have indicated that nanoemulsions have nano-sized droplets, a property which improves the sweep efficiency of oil in the reservoir. Researchers have also confirmed the high thermodynamic stability of nanoemulsions. Thanks to this property, immiscible liquids can reach a much greater distance into the formation. This significantly limits the adsorption of surfactants contained in the nanoemulsion, thus providing better protection against the re-trapping of oil. According to previous studies, to successfully approve the functionality of nanoemulsion, it is crucial to find the best formulation which provides the best properties, especially in terms of average droplet size. Studies have shown that nano-additives can significantly reduce interfacial tension between oil and aqueous solutions to as low as  $<0.001$  mN/m. Very good wetting of the rock also causes the phenomenon of spontaneous imbibition to micro-cracks, which helps to release extra oil. In addition, the nanoemulsion contains, in its composition, co-solvents in the form of citrus terpenes and isopropanol, which can further support the process of washing oil from the surface of the pores. The physicochemical properties of nanoemulsions suggest that they can be successfully used to recover the residual oil which is trapped in the fine pores and micro-fractures of reservoirs by capillary forces, even after primary and secondary recovery. In addition, the use of polymers with nanoemulsion can improve the displacement effect by using the mobility difference between oil and the displacement solution. The combination of these mechanisms improves the displacement efficiency in carbonate formations [27,28]. As previous studies have shown, the use of polymer-nanoemulsion flooding after polymer flooding can increase the recovery factor by more than 2%.

In this study, we examine the use of a new nanoemulsion formulation in carbonate rock for production support processes. This project was implemented by two cooperating research teams: the R&D center of Brenntag Polska, a producer and supplier of chemical materials for the petroleum industry, and a team of researchers from the Oil and Gas Institute—National Research Institute, as an independent scientific unit. The task of the first team was to prepare and pre-test the innovative nanoemulsion formulation, while the second team prepared and performed EOR tests on natural cores. The project was divided into several stages that can be briefly described as follows: preparation and initial testing of the emulsion formulation, checking the effectiveness of the EOR process in various conditions, and data analysis. By design, the nanoemulsion was developed to support the displacement of crude oil from high temperature carbonate deposits. Oil reservoir carbonate rocks are characterized by double porosity and often mixed wettability [29–31]. In this case, the most important physical phenomena affecting the efficiency of the technology being prepared should be considered. In the presence of fracture porosity, equal front displacement of oil is largely difficult to maintain, which is the basis of the efficiency of the process. The solution here may be to reduce the mobility of the displacement solution, which can be achieved by using a polymer additive. The second challenge to be addressed is improving the penetration of the displacing solution into the micro-cracks and small pores. An innovative method of using surfactants involves their preparation in the form of nanoemulsions which, apart from significantly improving wettability and reduction of surface tension, significantly reduce the adsorption of the active substance on the surface of the deposit rock. In the present research, polymer solutions and a newly developed nanoemulsion are used for the EOR process. With this combination, both necessary mechanisms were used for effective displacement; that is, improved wettability and reduced mobility

of the displacing solution [32–34]. Development studies, which are the subject of another publication being prepared, concerned the preparation of the formulation composition, development of a method for producing the nanoemulsion, and preparation of the polymer suspension. The products were selected by performing screening tests. For the nanoemulsion, parameters such as critical micelle concentration (CMC), surface tension, relative viscosity, density, separation time, thermal resistance, flash point, and freezing point were determined. The viscosity and thermal resistance of the polymer suspension were tested. After the initial stage, 23 out of 37 nanoemulsions and seven out of seven polymers were selected for further research. In the next stage, the effects of salinity, thermal stability, adsorption, and rheological properties were examined. The results of these studies allowed for recommendation of 10 nanoemulsion formulations and two polymer suspensions. Further work involved the testing of polymer-nanoemulsion systems. Twenty systems were tested by changing the polymer and nanoemulsion concentrations and testing the stability of the system at high temperature and salinity, determining wettability, surface tension, and dispersion. As a result of these tests, five polymer-nanoemulsion systems were selected and tested for stability in contact with oil. The testing of these systems occurred in two stages; on their basis, the most stable polymer-nanoemulsion system was finally selected. The research presented in this publication was conducted with their use. The purpose of this research was to perform laboratory tests and develop an effective technology for reservoir waterflooding using the tested and selected polymer and nanoemulsion. They were tested under conditions related to the real carbonate reservoir for which the waterflooding strategy is being developed. The reservoir's rock is dolomite and the deposit is characterized by high temperature. The oil and gas from this reservoir are characterized by a high content of hydrogen sulfide. Therefore, the purpose of the research was to check the polymer's resistance to high temperature and the presence of hydrogen sulfide. Studies of rheological characteristics confirmed its high resistance to contact with hydrogen sulfide, which ensures sufficient viscosity of the polymer solution and mobility contrast when displacing oil. The conducted tests determined the degree and dynamics of surfactant adsorption during laboratory waterflooding experiments through the presented data. The use of live oil recombined in PVT conditions for real reservoir conditions is unique in the presented research. To make the experiments even closer to the real process, the reservoir water was mixed with tap water, which is one of the variants considered for this field. The presented results of the laboratory tests are an important element for planned computer simulations of EOR processes in reservoirs and conducting pilot tests.

The tests performed on cores in reservoir conditions were aimed at confirming the effectiveness of the use of the polymer system combined with the newly developed nanoemulsion in EOR processes.

## 2. Materials and Methods

### 2.1. Materials

The tests were conducted with the use of natural carbonate cores, crude oil and natural gas, and reservoir water for the preparation of process solutions as well as polymer and nanoemulsion solutions. Core samples were provided by the Kocurek Industries Hard Rock Division (Caldwell, TX, USA). They were 3.81 cm (1.5-inch) core plugs made of Guelph Dolomite rock. The basic data of these cores are summarized in Table 1.

**Table 1.** Guelph Dolomite core plugs general data.

Core Name	Formation	Dolomite Content (%)	Quartz Content (%)	UCS <sup>1</sup> (Psi)
Guelph Dolomite	Sylurian	99.4	0.6	9000–12,000

<sup>1</sup> Uniaxial compressive strength.

Live oil was used for the research. Dead light crude oil and gas were recombined to create live oil in deposit conditions—that is, at a temperature of 120 °C and pressure of 38 MPa—with the use of a

Chandler Engineering (Tulsa, OK, USA) PVT system. The results of the analysis of dead oil, gas, and live oil parameters are presented in Tables 2–4, respectively.

**Table 2.** Gas analysis: main components.

Gas Type	C <sub>1</sub> –C <sub>6</sub> (mol %)	C <sub>7</sub> –C <sub>12</sub> (mol %)	H <sub>2</sub> (mol %)	N <sub>2</sub> (mol %)	CO <sub>2</sub> (mol %)	H <sub>2</sub> S (mol %)
Separated from oil	60.234	1.013	0.406	30.295	0.077	7.975

**Table 3.** Dead oil composition analysis.

Sample Number	Density (g/cm <sup>3</sup> )	Viscosity (mPa·s)	Asphaltenes (%)	Resins (%)	Saturated Hydrocarbons (%)	Aromatic Hydrocarbons (%)
R206/09/17	0.841	82.1	0.21	4.86	42.10	5.93

**Table 4.** PVT data of crude oil used for core floods experiments.

Type of Oil	Temperature (°C)	Pressure (MPa)	Density (g/cm <sup>3</sup> )	GOR <sup>1</sup> (sm <sup>3</sup> /m <sup>3</sup> )	Oil Volume Factor (m <sup>3</sup> /m <sup>3</sup> )
Live	120	38.0	0.726	166.8	1.56
Dead	23.5	0.098	0.841		1.00

<sup>1</sup> Gas to oil ratio.

To prepare the solution for displacement, reservoir water was used. For EOR testing, the reservoir water was then diluted with tap water in varying proportions, which is one of the considered real strategies for waterflooding of the reservoir. A general analysis of the reservoir water used is provided in Table 5.

**Table 5.** Reservoir water analysis.

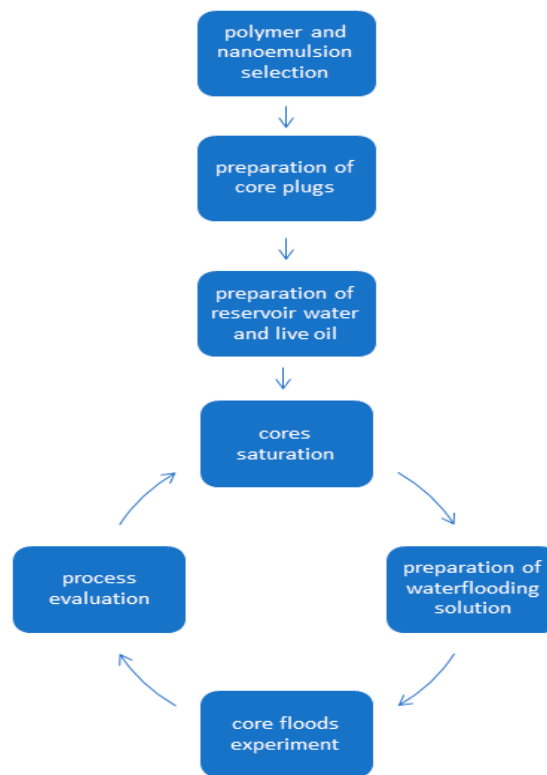
Density (g/cm <sup>3</sup> )	Basic Ions			
	Chloride (mg/L)	Bromide (mg/L)	Sodium (mg/L)	Calcium (mg/L)
1.214 <sup>1</sup>	213,493.14	1837.82	103,637.86	40,859.94

<sup>1</sup> Density at temperature 22 °C.

Polymer solutions with the trade name TN-16988 and the nanoemulsion D66 were provided for testing by a producer of chemical additives for the petroleum industry. The polymer used in this study was a copolymer of AMPS (2-acrylamido-2-methyl-1-propanesulfonic acid) and acrylamide. This polymer is well soluble in water anionic additives, as well as resistant to high salinity and high temperature. The nanoemulsion was based on terpenes, propan-2-ol, and a surfactant. As a result of previous research into the selection of the polymer and formulation of an innovative nanoemulsion for use in EOR technologies (as described above), these products were recommended for displacement tests. The manufacturer's goal was to produce products which are stable at high salinity and high temperature. It was also considered important that nanoemulsion components displayed proper dispersion and that the polymer suspension was stable under test conditions. The creation of a stable nanoemulsion–polymer system was also a key parameter. After testing many nanoemulsion and polymer formulations, the manufacturer recommended the two abovementioned products for laboratory testing of oil displacement efficiency from natural cores in simulated reservoir conditions.

## 2.2. Methods

The adopted research concept is shown in Figure 1.

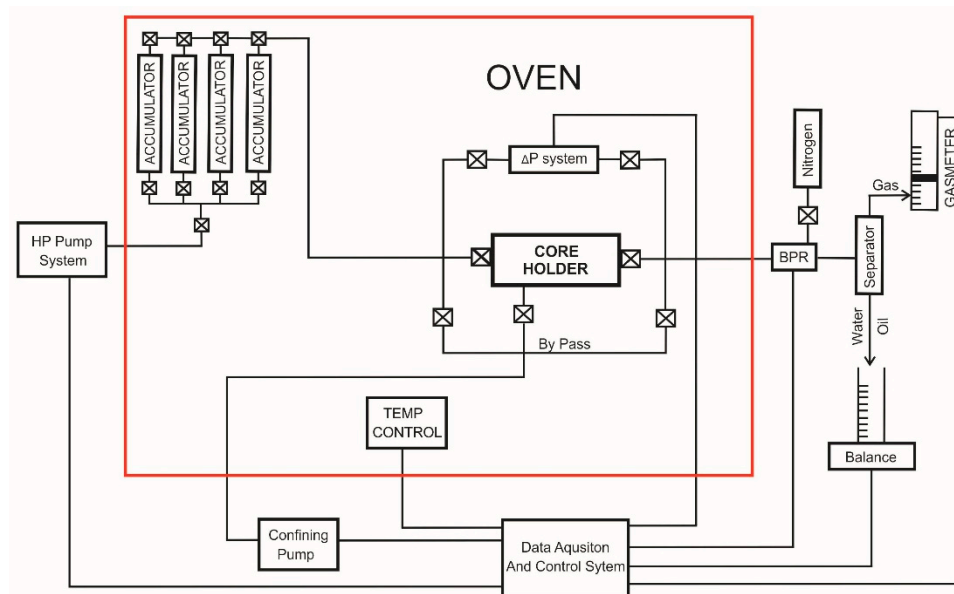


**Figure 1.** Flow chart diagram of the research.

In the flow chart diagram, the first part represents the preparatory work. Selection of the polymer and nanoemulsion were carried out based on previous research. Then, an appropriate amount of core material was prepared and tested, followed by reservoir fluids (i.e., brine and live oil). The next stage of work was cyclical activities, consisting of saturating the cores, preparing the displacement solution, conducting a core flooding experiment, and evaluating at the final stage. After each of the cyclical stages, the displacement solution was modified.

### 2.2.1. Core Sample Preparation

The core material was supplied in the form of core plugs with diameter of 3.81 cm and length of approx. 51 mm. These cores were used for testing the contact angle of the tested nanoemulsion and for core flood tests. Contact angle measurements were carried out on discs with a height of several millimeters cut from the core plugs. The front surfaces of these discs were ground and smoothed. After their preparation, the core plugs were cleaned by extraction in a Soxhlet apparatus using a set of different solvents and then rinsed in deionized water [35,36]. After purification, the core material was dried at 115 °C until a constant weight was obtained. Some cores prepared using this method were intended for core flooding tests and some for wetting angle tests. For core flooding tests, the cores were saturated with reservoir fluids (reservoir water and dead oil). This was achieved using a vacuum pump and chamber (reservoir water) and the Core Lab (Tulsa, OK, USA) AFS-300 coreflooding system for flow tests. A diagram of the device is shown in Figure 2.



**Figure 2.** Diagram of the AFS-300 coreflooding system.

After vacuum chamber saturation, the cores were placed in a Hassler core holder and then connected to the flow system and sealed. Reservoir water flow started through a set of cores while increasing the temperature and pressure in the cores (120 °C and 38 MPa, respectively). After stabilizing the conditions, 3 pore volume (PV) reservoir water was pumped at a rate of 0.3 mL/min. Subsequently, the pumping of dead oil at the same rate started. After obtaining an outflow of pure oil from the core (without reservoir water), another 3 PV of oil was pumped in, determining the saturation with oil and reservoir water, after which the core holder was closed for several hours to determine the adsorption balance. After this, the temperature and pressure were slowly lowered and the cores were removed from the core holder and placed in a pressure vessel filled with dead oil. After closing, a pressure of about 38 MPa was created in the vessel, which was placed in a heat chamber at 120 °C for two weeks. After this, the cores were ready to use for core flooding tests.

### 2.2.2. Core Sample Permeability and Porosity Measurement

Absolute permeability was measured with a DGP-100 gas permeability meter (EPS, Aberdeen, U.K.). The measurements were recorded on 3.81 cm diameter core samples. The core was placed in a Hassler core holder and then sealed in a rubber sleeve with external pressure. After sealing, nitrogen was flowed through the cores, measuring its flow rate and pressure difference before and after the core after the flow had stabilized. Based on these measurements, knowing the core dimensions, temperature, and current atmospheric pressure, the permeability coefficient was calculated.

The effective porosity of the cores was measured using an HPG-100 helium porosimeter and a BVMS 1000 unit for determining the total volume of samples; both units were produced by EPS (Aberdeen U.K.). The measurements were recorded on 3.81cm cylindrical cores. The measurement consisted of placing a rock sample in a sealed chamber of known volume and the expansion into the chamber of a constant volume of helium under fixed temperature and pressure conditions. The measured pressures before and after helium expansion allowed for calculation of the volume of the rock matrix with closed pores. After determining the entire volume of the same sample, the porosity coefficient could be determined.

### 2.2.3. Surface Tension and Contact Angle Measurement

The contact angle and surface tension values for individual solutions were tested using a goniometer (OCA 15EC, DataPhysics, Filderstadt, Germany). To measure the surface tension, solutions of D66 test

concentrations were prepared. The test liquid was placed in a syringe tipped with a needle and placed in the dispensing mechanism of the apparatus, forming liquid droplets in the lower part of the dispensing needle at a rate of 0.1  $\mu\text{L/s}$ . The surrounding medium was air. The measurement was repeated 20 times. The shape of the drop was the result of the superposition of two forces: the forces of gravity lengthened the drop and surface tension kept the drop in a spherical shape to minimize its surface. A characteristic parameter for the balanced state is the roundness of the drop shape. The balance of forces was determined mathematically using the Young–Laplace equation.

The contact angle was measured using the sessile drop method. Measurements were recorded on plates of cut rock, mechanically treated by sandpaper of varying granulation until a smooth surface was obtained, and cleaned from rock dust with compressed air. A drop of the test liquid (dead light crude oil or D66 solutions) was placed on the rock material by dispensing the liquid from a syringe with a needle. The drop was illuminated by scattered light and placed on the optical axis of a camera to visualize the boundary line. The contact angle was determined on the basis of computer analysis of the photograph captured after the adsorption equilibrium was established. The contact angle was measured inside the drop phase. The volume of the measuring drop was 5  $\mu\text{L}$  and 10 drops were applied and measured.

#### 2.2.4. Viscosity Measurement

Most natural and synthetic polymers have a variable dynamic viscosity coefficient depending on the flow rate. The addition of a polymer to an aqueous solution means that the resulting solution exhibits the characteristics of a non-Newtonian liquid. Its viscosity changes with the shear rate. The dynamic viscosity coefficient is best described by Equation (1):

$$\mu = K\dot{\gamma}^{(n-1)} \quad (1)$$

where  $\mu$  is the dynamic viscosity coefficient ( $\text{mPa}\cdot\text{s}$ ),  $K$  is the consistency index ( $\text{mPa}\cdot\text{s}^n$ ),  $\dot{\gamma}$  is the shear rate ( $\text{s}^{-1}$ ), and  $n$  is the power law coefficient.

Rheological characteristics were assigned using laboratory knowledge of the  $K$  and  $n$  values. Knowing these parameters, the viscosity of solutions could be calculated under given flow conditions (shear rate). Rheological tests were performed on a Nordman high pressure high temperature HPHT rheometer (Nordman Instruments Inc., Houston, TX, USA) at 120  $^{\circ}\text{C}$ . Measurements and rheological characteristics were determined in accordance with ISO 13503-1: 2011 (E) [37].

Important factors influencing the viscosity of aqueous polymer solutions are, among others, temperature and the presence of hydrogen sulfide. The viscosity coefficient decreases as the temperature increases. Hydrogen sulfide is a highly reactive reducing agent that, when combined with oxygen, can cause polymer chain degradation and loss of viscosity.

Considering the factors mentioned above, before performing EOR tests we decided to conduct tests on the rheological characteristics of the polymer and polymer-nanoemulsion solutions, considering the effects of temperature and the presence of  $\text{H}_2\text{S}$ . First, rheological measurements were recorded for the polymer and polymer solutions with the addition of the nanoemulsion. Then, samples of prepared solutions were placed in a pressure vessel in which a pressure of about 4 MPa was created using gas with a specific  $\text{H}_2\text{S}$  content. The samples were then placed in a thermostatic chamber at 120  $^{\circ}\text{C}$  for 7 days. After this, the solution in the container was cooled to ambient temperature and the rheological properties of the solutions were again measured.

#### 2.2.5. Core Flooding Tests

The dead crude oil pre-saturated cores were placed in a Hassler core holder, which was connected to the flow lines and control system of the AFS-300 coreflooding system. Then, the cores were sealed. Next, the dead crude oil flow was started by a set of cores with flow rate of 0.3 mL/min while increasing the pressure and temperature conditions adopted for the test. After their stabilization, the pumping of recombinant live oil from the pressure vessel was started under PVT conditions. At the outflow from

the cores, oil and gas were separated and their volumes were monitored. On this basis, the current gas/oil ratio (GOR) was determined. After obtaining a GOR value close to that obtained from PVT analysis, another 3 PV of live oil was pumped through the cores, constantly monitoring pressure, temperature, differential pressure, and oil and gas volumes. After pumping the required volume of live oil, the inlet and outlet valves of the core holder were closed and left under these conditions for several hours (overnight). Monitoring of reservoir fluids flowing from the cores allowed for possible correction of saturation of the cores with oil and reservoir water. The saturated cores prepared following this method enabled the planned EOR tests using various solutions and assumed displacement schemes.

### 3. Experimental Results

#### 3.1. Measurement of Porosity Coefficient and Permeability; Determination of Saturation with Reservoir Fluids

Laboratory tests began with measurements of the permeability coefficient and porosity of dolomite cores using DGP-100, HPG-100, and BVMS-1000 equipment. After determining these parameters, a physical model was prepared from the cores for EOR testing, which consisted of two cores with varying permeability. Subsequently, the cores were saturated with reservoir water and dead oil using the AFS-300 coreflooding system. The measurements are summarized in Table 6.

Table 6. Data of Guelph Dolomite core plugs used in core flooding tests.

Core Number	Test No.	Helium Porosity (%)	Nitrogen Permeability (mD)	PV <sup>1</sup> (mL)	So <sup>2</sup> (%)	Sw <sup>3</sup> (%)
BT1A BT1B	1	11.74 8.48	51.59 10.61	11.59	51.12	48.88
BT2A BT2B	2	12.56 10.64	113.00 11.05	10.92	54.01	45.99
BT3A BT3B	3	13.65 10.20	185.40 22.91	10.21	48.91	51.09
BT4A BT4B	4	12.98 11.62	116.40 57.58	11.90	59.66	40.34

<sup>1</sup> Pore volume of a set of two cores; <sup>2</sup> Oil saturation; <sup>3</sup> Water saturation.

Table 6 presents the Guelph Dolomite core measurements, which were used to test the efficiency of EOR processes using nanoemulsions. The measurements of the effective porosity coefficient indicated a relatively narrow range of values (from 8.48% to 12.98%). Therefore we concluded that, in terms of porosity, these cores showed high homogeneity. However, for the permeability coefficient, dozens of cores were tested and large differences in this parameter were found. The permeability coefficient varied from several to over 100 mD. Accordingly, we decided that the physical model for each EOR study would consist of two cores with different permeabilities such that the contrast in permeability was significant. On the inlet side in our model, the core with higher permeability was always placed first followed by the core with lower permeability. The physical dimensions of the cores were similar, which allowed us to obtain comparable porosity models with very similar pore volumes. The total pore volume available for reservoir fluids for physical core models varied slightly (from 10.84 to 11.90 cm<sup>3</sup>). Core sets for each study were saturated with reservoir water and oil, as described previously. The final saturation of the core set ranged from 48.91% to 59.66% for oil and from 40.34% to 51.09% for water.

#### 3.2. Measurement of Surface Tension and Contact Angle

The manufacturer developed a new D66 nanoemulsion for use in EOR processes. Based on the research conducted in preparing various formulations, three concentrations were recommended for core flooding tests: 1%, 2%, and 3%. These concentrations are relatively high. Literature data have indicated the possibility of using lower concentrations of surfactants, even at a level of 100 ppm [38].



Solutions for displacing crude oil from the cores were prepared on the basis of reservoir water (Table 5) diluted with tap water in a ratio of 1:10 (i.e., one volume of reservoir water was added to nine volumes of tap water). Nanoemulsion was added to the diluted reservoir water in order to obtain the selected concentrations. Surface tension was measured for these solutions; the reference surface tension for water was also determined. In one of the tests, the surface tension of the aqueous solution of the displacing liquid flowing out of the cores was also measured. These results may indicate the scale of surfactant adsorption on the pore surface. The contact angle of the prepared rocks was measured for the same nanoemulsion solutions, testing the contact angles of water and dead oil for reference. The results are shown in Tables 7–9, respectively.

**Table 7.** Surface tension.

Solution	Surface Tension <sup>1</sup> (mN/m)
Water	72.66
1% D66	30.89
2% D66	29.98
3% D66	28.01

<sup>1</sup> At 22 °C.

**Table 8.** Surface tension of outflowing solution from test 4.

PV	Surface Tension <sup>1</sup> (mN/m)
0	29.17
0.75	37.97
1.5	50.55
2.25	57.08
3.0	58.06
3.75	57.72
4.5	57.44
5.0	56.69

<sup>1</sup> At 22 °C.

**Table 9.** Contact angle on Guelph Dolomite surface.

Solution	Contact Angle $\theta$ <sup>1</sup> (°)
Water	69.45
Crude oil	12.86
1% D66	14.50
2% D66	8.65
3% D66	7.03

<sup>1</sup> At 22 °C.

The data showed that the D66 nanoemulsion significantly reduced the surface tension of diluted reservoir water. However, increasing its concentration in solution from 2% to 3% did not cause a measurable reduction in surface tension. Investigating the surface tension of the outflowing solution, it was found that the surface tension increased almost twice. This indicates the adsorption occurring on the surface of the rock. Some excess nanoemulsion may be necessary due to adsorption of the active substance on the rock surface during the displacement process. This was only verified after the EOR tests. Analysis of the measured contact angle of the dolomite rock surface showed that the surface was oil-wet (hydrophobic). The contact angle for water was several times higher than for oil. The addition of 1% D66 nanoemulsion to the diluted reservoir water reduced the contact angle to that of oil. Increasing the concentration to 2% further reduced the contact angle. However, further increasing the concentration to 3% was not very effective, as the consequent change in the contact angle was relatively small.

### 3.3. Measurement of Rheological Properties of Displacement Fluids

Rheological properties were measured for three different solutions. All were prepared using of reservoir water diluted with tap water (one part reservoir water and nine parts tap water). These fluids were 0.5% solution of TN-16988 polymer, 0.5% solution of TN-16988 polymer with the addition of 3% D66 nanoemulsion, and the same polymer-nanoemulsion solution placed for seven days in 120 °C with the presence of H<sub>2</sub>S-containing gas. The concentration of polymer and nanoemulsion in the performed tests was the highest of those planned for use in the EOR tests. The results of the study provided information about the impact of the addition of the nanoemulsion on the viscosity of the polymer and whether (and to what extent) the presence of hydrogen sulfide affected the rheological parameters of the solution. The test results are presented in Figure 3.

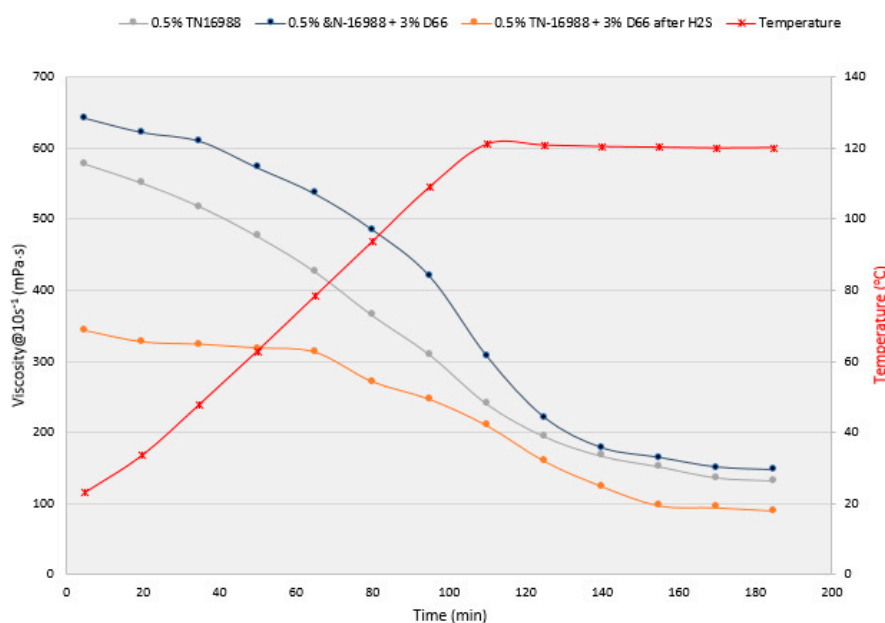


Figure 3. Rheological data of enhanced oil recovery (EOR) fluids.

For clarity, viscosity was calculated at the shear rate of  $10 \text{ s}^{-1}$ . The first phase of the test involved heating the samples to the test temperature of 120 °C. The viscosity of all solutions decreased during this time and stabilized after reaching the indicated temperature. The highest viscosity was characterized by a solution with the addition of both polymer and nanoemulsion. In the initial phase, at ambient temperature the viscosity was 643.7 mPa·s after reaching the peak temperature, dropped to about 221 mPa·s, and stabilized to 147.2 mPa·s by the end of the test. The solution prepared with only polymer added to the diluted reservoir water had a viscosity of 577.6 mPa·s at the beginning of the test and 132.5 mPa·s just before the end of measurement. The third curve characterizing the viscosity of the solution with the addition of the polymer and nanoemulsion exposed to temperature and hydrogen sulfide had a markedly lower viscosity than the others. A particularly large difference was observed at the beginning of the measurement at ambient temperature. The initial measured viscosity was 342.5 mPa·s. When heated, the viscosity of this solution was less than that of the solution not exposed to temperature and hydrogen sulfide. At the end of the test, its viscosity was 90.3 mPa·s.

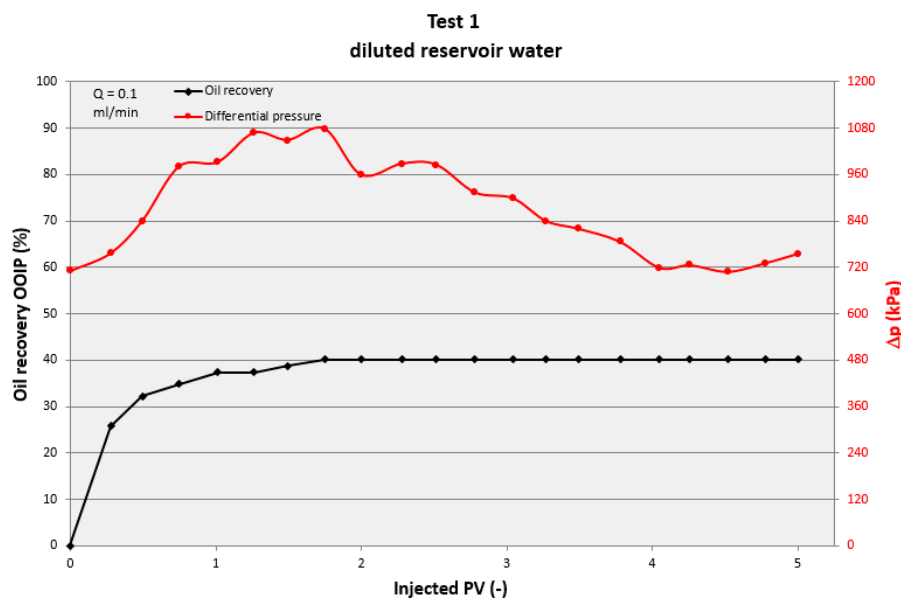
Based on the results, we found that the addition of the nanoemulsion to the polymer solution increased the viscosity. At 120 °C, this difference was small, around 14.7 mPa·s at a  $10 \text{ s}^{-1}$  shear rate. Hydrogen sulfide and temperature caused degradation of the polymer and, hence, reduced the viscosity of the solution. Under the test conditions, the viscosity at the end of the test decreased by 56.9 mPa·s, a decrease of approx. 38.6% compared to the solution not exposed to temperature and hydrogen sulfide.

### 3.4. Oil Displacement with Solutions with the Addition of the New Nanoemulsion

This part of the experiment was conducted on physical models from natural cores saturated with reservoir media in conditions similar to that of the reservoir. They were designed to confirm the effectiveness of the newly developed D66 nanoemulsion in association with the polymer in the EOR process. During the research project, several dozen displacement tests were conducted; in this paper, only a few of these results are presented. The first test was performed using a dilute reservoir water. In the second test, 0.3% polymer and 3% nanoemulsion were added to this water. In the third test, the polymer concentration was reduced to 0.02%, keeping a nanoemulsion concentration of 3%. The fourth and last test used the lowest polymer and nanoemulsion concentrations of 0.05% and 1%, respectively. The oil recovery factor data were reported after injection of 0.25 PV of the solution for all tests. Each test was completed after pumped of the 5 PV tested solution. The oil recovery coefficient and the differential pressure were monitored. The results of displacement efficiency are shown in Table 10 and Figures 4–7.

**Table 10.** Waterflooding experiments results.

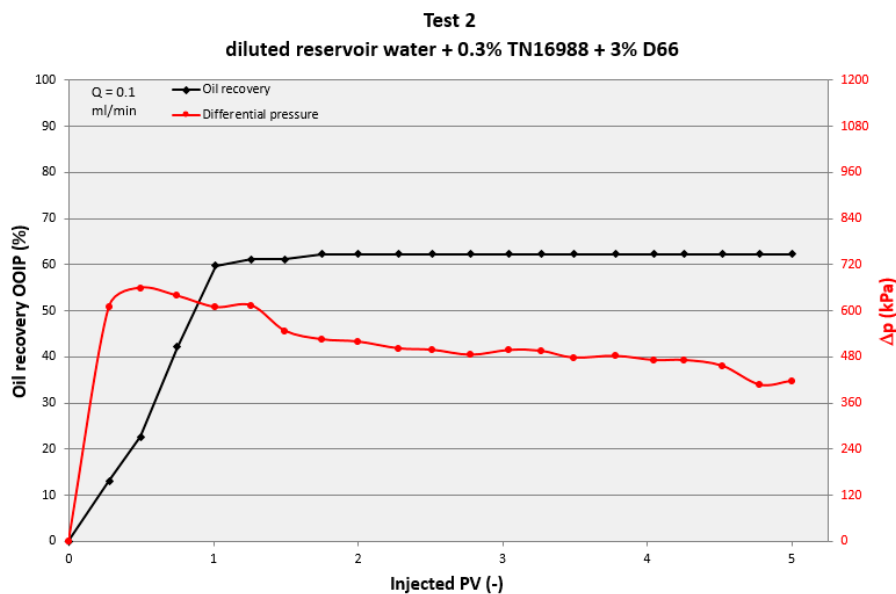
Test No.	Composition of Displacement Solution (%)	Final Recovery Factor (%)	Maximum Differential Pressure (kPa)	Final Differential Pressure (kPa)
1	Diluted reservoir water	40.1	1066	755
2	Diluted reservoir water +0.3% TN16988 + 3% D66	62.3	658	416
3	Diluted reservoir water +0.02% TN16988 + 3% D66	55.0	59	59
4	Diluted reservoir water +0.05% TN16988 + 1% D66	77.5	295	295



**Figure 4.** Recovery factor for diluted reservoir water.

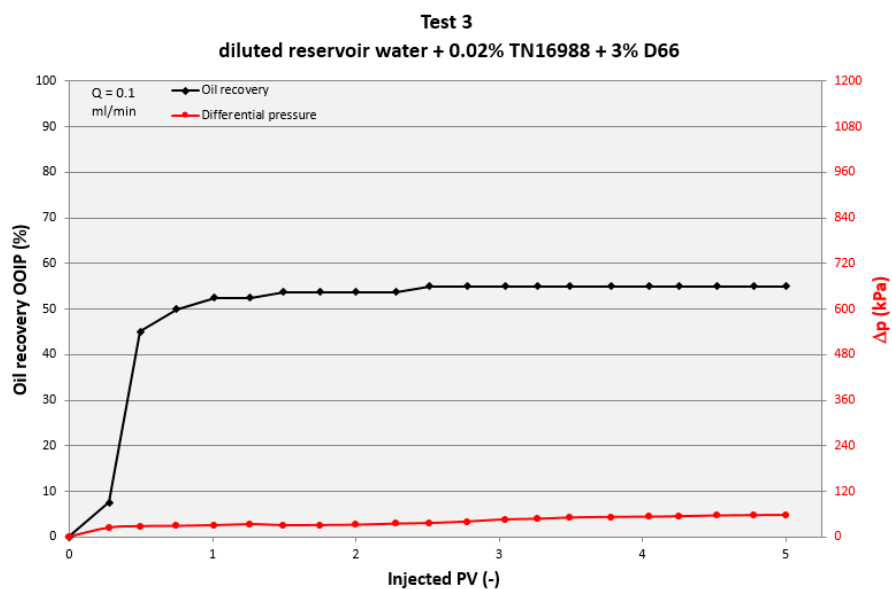
Figure 4 shows that the use of diluted reservoir water in the displacement process produced a low oil recovery slightly exceeding 40% original oil in place (OOIP). This was achieved after injection of approximately 1.5 PV displacement solution into the core. The differential pressure measured for the assumed flow was relatively high (at 1066 kPa) in the first part of the experiment. Then, after reaching final drainage, the pressure slowly lowered and stabilized at around 750 kPa. Two factors influenced the relatively high displacement pressure: the lower permeability of the core plugs compared to

the core plugs used in other tests and the lack of additives reducing flow resistance (i.e., polymer or nanoemulsion).



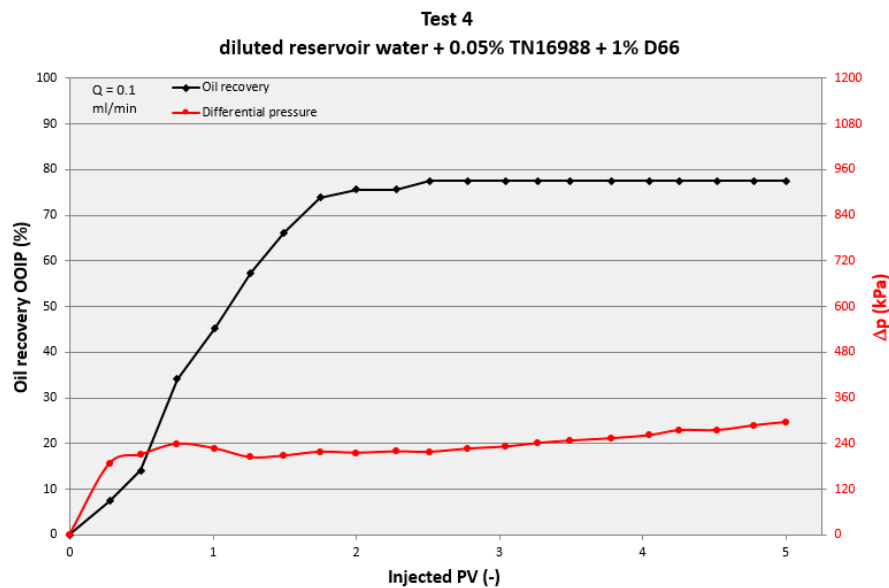
**Figure 5.** Recovery factor for diluted reservoir water with the addition of 0.3% polymer and 3% nanoemulsion.

In test two, 0.3% TN-16988 polymer and 3% D66 nanoemulsion were added to the prepared diluted water. This resulted in an increase in the oil recovery to 62.3%, while reducing the differential pressure to 658 kPa at the beginning and 416 kPa at the end of the process.



**Figure 6.** Recovery factor for diluted reservoir water with the addition of 0.02% polymer and 3% nanoemulsion.

The results of the test shown in Figure 6 were obtained with a polymer concentration of 0.02% and the same concentration of nanoemulsion as used in the previous test (3%). The oil recovery factor decreased to a final value of 55.0%; 7.3% lower than at the higher polymer concentration. However, a lower differential pressure, reaching a maximum value of 58.8 kPa, was observed.



**Figure 7.** Recovery factor for diluted reservoir water with the addition of 0.05% polymer and 1% nanoemulsion.

The last of the presented tests produced the best results of the whole series of tests. They were achieved with polymer and nanoemulsion concentrations of 0.05% and 1%, respectively. With this displacement fluid, an oil recovery of 77.5% was obtained. The displacement process occurred more slowly than in previous tests and reached the maximum value after pumping over 2 PV. We concluded that such concentrations slow the displacement process, thereby increasing its effectiveness. The obtained recovery factor was 37.35% higher than without the addition of polymer and nanoemulsion. The differential pressure measured during the process reached a maximum of 295.5 kPa.

#### 4. Discussion

We performed studies to confirm the effectiveness of the application of EOR processes based on a polymer-nanoemulsion solution. The composition of this solution enables various process mechanisms to occur in the reservoir: the polymer stabilizes and aligns the displacement front, whereas the newly developed nanoemulsion improves the wettability of the pore surface and its penetration. Model laboratory tests were performed on Guelph Dolomite cores, using reservoir water, live oil, and the tested additives—polymer TN-16988 and nanoemulsion D66. The partial research results of the ongoing development of new products presented here provide a basis for formulating conclusions and planning further work.

Physical models for the displacement process included two cores, which were selected to have different permeabilities and similar pore volumes. As such, we achieved a similar saturation of the physical models with reservoir media.

The tests of surface tension and contact angle on the rock surface confirmed that the addition of the nanoemulsion significantly reduced their values. Determining the most effective concentration of this additive is also affected by agent adsorption on the rock surface.

Rheological property measurements of solutions with the addition of polymer and nanoemulsion confirmed that the proposed system has sufficient viscosity to affect the alignment of the displacement front. The measurements showed that the system is susceptible to hydrogen sulfide, but the viscosity loss was not high enough, so it cannot be used in carbonate rocks with high deposit temperatures.

The best EOR laboratory simulation results were obtained for polymer and nanoemulsion concentrations in the dilute reservoir water of 0.05% and 1%, respectively. In this case, the measured oil recovery was 77.5%, which was 37.5% higher than that obtained for water without additives. In the Test 2, high concentrations of polymer and nanoemulsion (0.3% and 3%, respectively) were used. A much

higher oil recovery factor (62.3%) was obtained than for water, with a relatively low differential pressure (definitely lower than that for water). Limitation of the polymer content to 0.02% in Test 3 caused a decrease in efficiency of more than 7% compared to Test 2. However, a much lower pressure drop was obtained, which may indicate less damage to the cores. Test 4, compared to Test 3, was performed with a slightly increased polymer concentration (0.05%) and a reduced nanoemulsion concentration (1%). The increase of differential pressure was noticeable, which may indicate deteriorating flow conditions through the cores. However, a significant oil recovery efficiency of 77.5% was observed, which seems very promising. Displacement occurred more slowly in this test, which may indicate the effect of nanoemulsion on better cleaning of the pore surfaces with respect to crude oil and its release from micro fissures. The differential pressure during this test was relatively stable and lower than that for water. Based on this study, this composition is recommended for further work. The next stages of this project will focus on computer simulations of the displacement process for a selected deposit. The final stage involves pilot work in selected wells. The results of all these activities can provide the basis for the implementation of this technology for wider use.

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## Nomenclature

EOR	Enhanced oil recovery
HPHT	High pressure high temperature
CMC	Critical micelle concentration
UCS	Uniaxial compressive strength
BPR	Back pressure regulator
GOR	Gas oil ratio
PV	Pore volume
OOIP	Original oil in place
$\mu$	Viscosity (mPa·s)
K	Consistency index (mPa·s <sup>n</sup> )
$\dot{\gamma}$	Shear rate (s <sup>-1</sup> )
n	Power law exponent

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