Article

Design of a Polymer Composition for the Conformance Control in Heterogeneous Reservoirs

Inzir Raupov [1,*] , Mikhail Rogachev [2] and Julia Sytnik [1]

1   Department of Petroleum Engineering, Saint Petersburg Mining University, 199106 St. Petersburg, Russia
2   Department of Petroleum Engineering, Ufa State Petroleum Technological University, 450000 Ufa, Russia
*   Correspondence: inzirrr@yandex.ru

Abstract: The article is devoted to the issue of a low sweep efficiency in the heterogeneous terrigenous reservoirs containing remaining oil. Water plugging operations that redirect the injection fluid flows into unswept zones, are one approach to enhancing the oil recovery in these reservoirs. The commonly used chemical reagents in these treatments are acrylate polymer solutions. The polymer solutions must reach the target water-saturated zones and form a strong gel barrier there. Furthermore, the polymer compositions should have a low initial viscosity to provide a good injectivity and penetration ability. Therefore, the methods of adjusting the gelation time are necessary. There are numerous studies in modern scientific society devoted to the study of water-plugging polymer compositions. However, aspects, such as the effect of the hydrogen index on gelation, have received insufficient attention. In this paper, we describe the features of the developed polymer composition, based on a hydrolyzed polymer of acrylonitrile with a controlled gelation time for the chemically enhanced oil recovery. The component composition and the concentration levels were selected, based on the alterations in the hydrogen index of the polymer solution. It was scientifically proven that by adhering to a neutral hydrogen index, it is possible to improve the properties of the polymer composition. Moreover, using a model of a heterogeneous reservoir, it was confirmed that the proposed polymer composition achieves selective plugging. As a result of the polymer gel treatment, the water cut decreased by 4% and the displacement coefficient of oil increased by 20%, in comparison with the effect of the original composition without a gel-time modifier.

Keywords: enhanced oil recovery; chemical EOR; gel treatment; conformance control; water cut; polymer composition; gel-time modifier; sweep efficiency improvement

1. Introduction

In 2020, a reserve base of the Russian Federation faced a change in the structure of "traditional" and "hard-to-recover" oil production. More specifically, the share of "hard-to-recover" oil in the total production volume became higher than "traditional" and achieved 54% (Figure 1).

The medium- and long-term prospects for the increasing oil production are associated with such hard-to-recover resources, as oil in Domanikov, Bazhenov, Kuonamskaya, and Khadumskaya formations [1], the Arctic shelf, the deep Jurassic, and Achimov formations, the residual oil from unique and large fields, and high-viscosity oils. In several papers [2–4], some issues of the Arctic shelf development and drilling to a deep depth in Russia, are discussed. In 2020, the largest share (47%) of the hard-to-recover oil fell on fields with a high degree of depletion (i.e., with more than 80% of the initial recoverable reserves extracted). In such conditions, terrigenous reservoirs in some fields in the West Siberian and Volga-Ural oil and gas provinces, are also being developed, using water flooding as a secondary method of the enhanced oil recovery (EOR). Oil deposits in this area are distinguished by their large size and relatively simple structure. However, their levels of depletion, on average, exceed 60%, and their water cut is also very high—94%, on

average [5]. Furthermore, these reservoirs are characterised by heterogeneity, in terms of their permeability.

"Hard-to-recover" oil production in Russia

Figure values (bars, Mt): 2014: 134; 2015: 164; 2016: 195; 2017: 208; 2018: 246; 2019: 255; 2020: 222.

Line values (Shale, %): 2014: 27; 2015: 33; 2016: 39; 2017: 41; 2018: 49; 2019: 55; 2020: 54.

Legend: "Hard-to-recover" oil production, Mt (bar); Shale of "Hard-to-recover" oil production in Russia, % (line).

Figure 1. "Hard-to-recover" oil production in Russia [6].

The remaining oil is located in areas that have not been previously drained or flooded. In order to tap into these reserves, conformance-improvement treatments are used in heterogeneous reservoirs. Therefore, polymer gel systems, prepared by polyacrylamides (PAMs), have been extensively used in water management [7,8]. Some of the polymer gel systems have been observed in [9] for use in water shut-off operations and in [10,11] for use in well killing operations.

Fundamentally, PAMs have good performance indicators, among which are:

- a decrease in the water cut, due to selective properties;
- an increase in the oil production, due to the water flow redirection into previously unswept oil-saturated zones with a low permeability.

The experience of using conformance-improvement treatments at various stages of the field development, has shown that the success of their application depends on the level of the reserve depletion. The higher it is, the smaller its effect on the oil production [12,13]. Re-treatments also reduce their effect. An analysis of the crosslinked polymer systems re-treatments, radiation crosslinked polyacrylamides, and the temperature resistance gels in terrigenous reservoirs located in the Volga-Ural and West Siberian oil and gas provinces, showed that the specific effect decreased from 2 to 14 times [14,15].

The decrease in the efficiency can be explained by the fact that when these technologies are used repeatedly, the low-concentrated polymer composition starts degrading, due to its low structural strength, and the water flows rarely reach to unswept zones, due to the low effective penetration of the highly concentrated gels.

It is considered optimal to use water plugging compositions with a low initial viscosity and high strength, which can be achieved by adding a gel-time modifier to a highly concentrated polymer composition.

For convenience in navigating the paper, it is proposed to use the flow-chart (Figure 2).
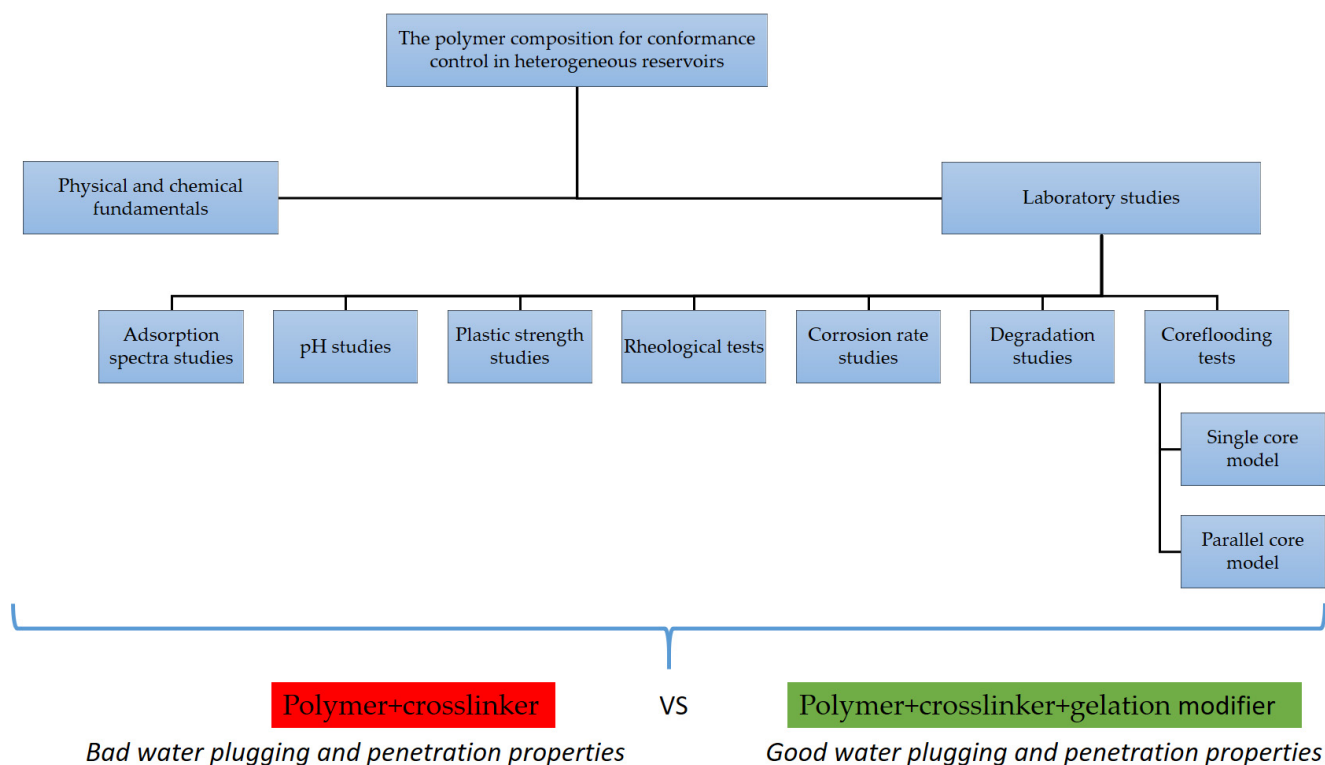
Figure 2. Enlarged research methodology.

2. Physical and Chemical Fundamentals

There are different ways to reduce the initial viscosity of the polymer composition that also leads to an increase in the gelation time:

- a molecular weight reduction of PAMs. The optimal molecular weight is considered to be in the range of 12 to 15 MDa. However, the reduced molecular weight can lead to the increased PAM concentration in the solution, to obtain the desired physicochemical and mechanical properties of the polymer composition;
- an increase in the salinity. In high-salinity water, the residual resistance factor decreases because of the polymer degradation [16];
- a decrease in the concentration of chemical reagents. As noticed above, a decrease in the concentration of the polymer causes a decrease in its strength and gel degradation;
- adding a gelation inhibitor. It is considered one of the most promising ways to reduce the viscosity and improve the physicochemical and mechanical properties of the polymer composition;
- dynamic injection. The selection of the optimal injection rate for the polymer composition was based on determining the range of the shear rates at which the effective viscosity of the water plugging composition would be the lowest [17]. An increase in the shear rate leads to an increase in the elastic deformation and may also lead to an increase in the complex viscosity. The upper limit of the injection rate value also depends on the fracturing pressure;
- a decrease in temperature. The only effect here is an increase in the gelation time.

Therefore, the best solution for the production of the high-strength gels with a low initial viscosity is the use of chemicals, such as gel-time modifiers, gelation delayers, water repellents, and polymers that have been exposed to radiation [18,19]. Using polymer compositions with the above mentioned additives will lead to an increase in the strength of the watertight barrier, due to the injection of the composition with a high polymer concentration into the formation to a sufficient depth.

Despite the numerous benefits of these compositions, there are some drawbacks:

- the use of the organic acids as gelation delayers reduces the viscosity and increases the gelation time while decreasing the plastic strength;
- the use of water repellents reduces both the critical shear stress and the adhesion of the polymer composition to the hydrophilic rock, which can make the gel too mobile and cause it to be removed from the formation;
- the exposure of the polymer molecules to radiation is a promising method that allows for the synthesis of the crosslinked polymer particles with sizes up to 100 nm, which can increase the depth of the polymer penetration into the formation. However, this method is technologically sophisticated, laborious, and energy-intensive.

The selection of the component composition was based on an analysis and review of sources on organic chemistry and polymers [20,21]. Polyacrylonitriles, as most important synthetic polymers, are produced by the chain-growth polymerization. In contrast to the step-reaction polymerization, polymers grow very quickly in the chain-growth polymerization. The polymerization rate in this case can be decreased by adding hydrochloric or sulfuric acid. Furthermore, polymerization slows down in the presence of acetic acid, acetaldehyde, succinonitrile, 1,3-butadiene acetylene, octariene-1,3,7-yna-5-vinyl acetylene, and hydroquinone monoalkyl esters, and it is completely inhibited by trans-dibenzoylethylene. In the oil industry, hydrochloric acid has become widely used, in particular as a pH reducer.

Moreover, there are a number of saponifying agents: NaOH (1% solution), HCl, HCOOH, Na_2CO_3, H_2SO_4, and H_3PO_4. In this series, the following should be used as gel-time modifiers: hydrochloric acid to slow down the gelation process and sodium hydroxide as a neutralizer to increase the pH of the polymer composition to neutral.

From a chemical point of view, a decrease in the viscosity of a HPAM or HPAN solution caused by adding a strong monobasic acid and an increase in strength and viscosity caused by adding a metal hydroxide, can be explained as follows. In an acidic environment, the degree of dissociation of the polymer electrolyte macromolecules decreases, due to the formation of the weakly dissociating groups of polyacrylic acid, which makes polymer molecules fold into dense coils and, as a result, a decrease in the effective viscosity and the injection pressure gradient can be seen (Figure 3). When the pH is increased by adding alkali, the amide groups of the polymer are hydrolyzed. The hydrolyzed polymer of the acrylic series dissociates in water, cleaving off the cation. The resulting negative charges along the molecules contribute to the production of the long macromolecules of the substance (under the influence of the Coulomb repulsion between the charged groups in the chain). The long, chain-like molecules contribute to a significant increase in the viscosity of the polymer composition, which will lead to the formation of a durable gel barrier.


(**a**)　　　　　　　　　　　　　　　　　　　　　　(**b**)

Figure 3. Acrylic polymer macromolecules in a neutral medium (closer to pH = 5–6)—(**a**); in an acidic medium—(**b**) (pH < 1).

The interaction of the components used in the polymer composition, where $AlCl_3$ is used as a crosslinker, hydrochloric acid HCl is used as a gelation delayer, and sodium hydroxide NaOH is used as a neutralizer, is as follows:

- when a strong monobasic acid (such as hydrochloric acid) is added to water, HCl dissociates into the H^+ cation and the Cl^- anion, resulting in an excess of H^+ protons in the system and a decrease in pH:

$$HCl \leftrightarrow H^+ + Cl^- \tag{1}$$
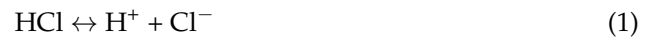
- the addition of HPAN to the HCl solution causes polyacrylonitrile to hydrolyze, resulting in the formation of a carboxyl group and its reaction products (ammonium hydroxide):

$$\text{(C≡N)}_n + H^+ + H_2O \rightarrow \text{(C=O, OH)}_n + NH_4OH \tag{2}$$
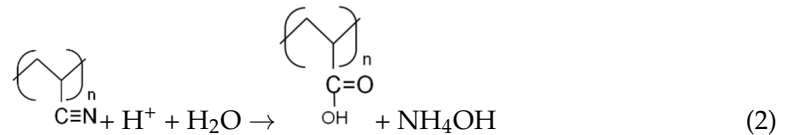
- due to the fact that NH$_4$OH is an unstable compound, it decomposes into ammonia and water. This becomes evident from the pungent smell of ammonia:

$$NH_4OH \rightarrow H_2O + NH_3\uparrow \tag{3}$$

- since the crosslinker in an acidic medium dissociates into the cation Al^{3+} and the anion Cl-, the precipitate Al(OH)$_3\downarrow$ is not observed. This allows the Al^{3+} cations to interact with the polymer molecules. However, due to the fact that the polymer molecules are in a compressed state, the cations of the polyvalent metals are blocked from entering the coil. So, the crosslinking process occurs only on its surface. This is the reason why there is no sharp increase in viscosity that is characteristic of the polymer crosslinking process. Instead of the Al^{3+} cations, the Cr^{3+} or Fe^{3+} ions can be used.

$$\text{(C=O, OH)}_n + Al^{3+} + Cl^- + Cl^- + Cl^- \rightarrow \text{(crosslinked Al complex)} + 3HCl \tag{4}$$
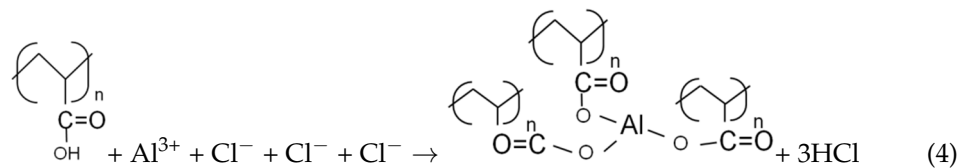
To neutralize the polymer solution containing hydrochloric acid, an alkali solution (for example, NaOH) is injected into the formation before the polymer gel treatment.

3. Material and Methods

The proposed polymer composition consists of the water soluble polymer (HPAN), the crosslinker (chromium acetate), and the gel-time modifier (delayer, hydrochloric acid, and neutralizer, sodium hydroxide). According to GOST 4328-77, the alkali is represented by sodium hydroxide. Polyvalent metal salt (chromium acetate trivalent) is used as a crosslinker, according to TU 2436-005-75911280. According to GOST 3118-77, the gelation delayer is represented by a strong monobasic acid, hydrochloric acid.

As a saturating and displacing liquid, a model of the reservoir water was used, prepared according to a 6-component analysis of the reservoir water in the terrigenous Devonian deposits of the X oil field. The salinity of the reservoir water is 125,914 g/L.

To design a model of a heterogeneous formation, dry quartz sand from the Muraevnya mining and processing plant of a 0.5–0.8 mm fraction was used to create a highly permeable reservoir model, and the fractions of 0.16 mm were used to create a low-permeable reservoir model.

A model of oil is represented by the oil from the Devonian deposits in field X. The kerosene TS-1, according to GOST 10227-86, was used for the core flooding tests.

The experimental part is carried out under reservoir-like conditions, including a reservoir temperature (40 °C) and the salinity of the reservoir water (125,914 g/L).

In the core flooding tests, the flow rates are selected, based on the actual flow rates of the injection at the object of study, oil field X.

3.1. Absorption Spectra Study

In order to determine the types of bonds appearing in the gelation process, the structures of the organic compounds in the polymer composition were studied using Raman spectrometry. Raman spectra were recorded between 3700 to 150 cm^{-1} on a Thermo Scientific Nicolet iS 50 FT-IR spectrometer. The Omnic Spectra software was used to interpret the results of the test. The bonds that formed were analysed, based on [22,23]. The studies to determine the emerging bonds were carried out for the crosslinked compositions, and they were compared with the basic Raman absorption spectra of the initial compositions.

3.2. Hydrogen Index Study

When the pH value of the acrylic polymer reaches 10–12, the imide bridges are broken down (for example, the acrylic acid imide -C$_2$H$_3$COOH-NH-C$_2$H$_3$COOH-), which leads to a decrease in the strength of the polymer composition. Therefore, the water-soluble acrylate polymers have a maximum viscosity in the neutral zone. In this regard, it is important to keep the pH of the polymer composition neutral in the formation.

The component compound concentrations of the gel-time modifier (the gelation delayer, hydrochloric acid, and the neutralizer, sodium hydroxide) were selected by measuring the pH of the polymer composition with the addition of each of the gel-time modifier components. The acidity was found using a Mettler Toledo Seven Easy S20K pH meter.

3.3. Plastic Strength Research Method

We used Rehbinder's conical indenter method to determine the plastic strength of the polymer composition. This method is based on the immersion of a cone (with an angle of the axial section of the cone at the apex equal to 60°) with a known mass in the system under study under a constant load [24,25]. The plastic strength (P_s) was calculated using the following equation system:

$$\begin{cases} P_s = K_a \times \frac{F}{h^2} \\ K_a = \frac{1}{\pi} \times cos^2\left(\frac{\alpha}{2}\right) \times ctg\left(\frac{\alpha}{2}\right) \end{cases} \tag{5}$$

where

P_s is plastic strength, Pa;
α is the angle of the axial section of the cone at the apex, equal to 60°;
K_a is a coefficient depending on the angle of the axial section of the cone at the apex, unit fraction;
F is the weight of the submerged system, N;
h is the depth of immersion of the cone in the gel, m.

3.4. Rheological Study

The main criteria for selecting the optimal water plugging composition are the gelation time, the mechanical shear strength of the gel (the value of the initial pressure gradient), and the technological stability properties of the gel in the reservoir conditions.

The gelation time in a dynamic state (during the movement through pipes and injection into the formation) is found by measuring the effective viscosity μ_{eff} of the polymer composition over time. Following a certain period of time, μeff increases sharply, which is associated with the formation of a strong elastic gel structure. This time is called the gelation time. A gelation onset time is defined as the time when the viscosity builds up. The moment when the viscosity stops growing or its growth rate changes is called the time of the end of gelation.

The effective viscosity was measured at a constant velocity gradient (shear rate $D = 44$ s^{-1}), depending on the time using a Rheotest RN 4.1 universal rotational viscometer and a cylindrical measuring system. The polymer layer thickness was 5.225 mm.

The rheological properties were found, based on GOST 25276-82.

3.5. Corrosion Rate Study

The laboratory studies of the corrosion rate were carried out using the gravimetric method, according to GOST 9.506-87. Steel plates (St3 of Russian GOST 380-2005) with dimensions of 50 mm × 10 mm × 0.5 mm (*HxWxD*) were used as a corrosive material. The experiment was conducted over a period of 24 h. The corrosion activity was measured under two conditions: at standard temperature $T = 20\ °C$ and at $T = 105\ °C$.

3.6. Degradation Study

Strong acids and alkalis have a disintegrating influence on the polymer compositions. Strong acids can break down the polymer bridges and chains. As destructing agents, we used HCl, HNO_3, CH_3COOH, HCOOH, and H_2O. The destructive force of these agents was found, based on OST 39-231-89. The study consisted of assessing the change in the polymer mass before and after exposure to a destructing agent [26].

3.7. Plugging Efficency Evaluation through the Core Flooding Test

The plugging efficiency of the proposed polymer composition was estimated through two types of core flooding tests: using a single core model and a parallel one.

3.7.1. Single Core Model Test

The core flooding test with a single core model (Figure 4) was performed to examine the polymer composition plugging efficiency with (core samples No. 4, 10, 14, 9, and 13) and without the gel-time modifier (core samples No. 1, 2, 3, 7, and 8) on sand packed tube cores with an equal grain distribution as in oil field X. At the beginning of this experiment, some characteristics were measured and estimated: the weight of the samples, the geometry measurements, porosity (*m*), and permeability of gas (absolute permeability, K_{abs}) in the conditions close to the reservoir.

Then, the core samples were placed into a saturator and flooded with water under a vacuum. As soon as the samples were saturated, they were weighed, and the pore volume (*PV*) was estimated. Following that, the cores were flooded with kerosene and then with crude oil, to create the residual water saturation and initial oil saturation. Finally, the core samples were flooded with water to create the residual oil saturation.

Subsequently, the core samples (only No. 4, 10, 14, 9, and 13) were flooded with the alkaline solution in the amount of one pore volume at a constant flow rate ($Q = 0.5\ mL/min$). The effective permeability of the alkaline solution was measured. The flooding was carried out in the "forward" direction.

Then, the investigated polymer gel composition was injected (with a crosslinker and polymer ratio volume of 1:10) in the amount of 1 *PV* at a constant flow rate ($Q = 0.5\ mL/min$). The stabilised pressure gradient (shear pressure gradient of polymer composition) was recorded, and the mobility ratio was calculated, based on Darcy's law. Furthermore, the resistance factor (*RF*) was estimated.

Following the gel placement, the pressure gradient was stable, and the post water injection at different flow rates was carried out in order to determine the extent at which the polymer composition reduced the effective permeability. The next step of this experiment was to estimate the residual resistance factor (*RRF*).

3.7.2. Parallel Core Model Test

the core flooding tests were designed and conducted using a parallel core model (Figure 4) to create the conditions of a vertical heterogeneity. There were two types of sand packed tube cores (with a diameter of 3 cm and length of 6 cm for each core) in the parallel core flooding unit: with high and low permeability.

The main purpose of this part of the experiment was to determine a displacement efficiency before and after treatment, and also a water cut reduction efficiency by the developed polymer gel with (core samples No. 1A and 1B) and without (core samples No. 2C and 2D) the gel-time modifier.
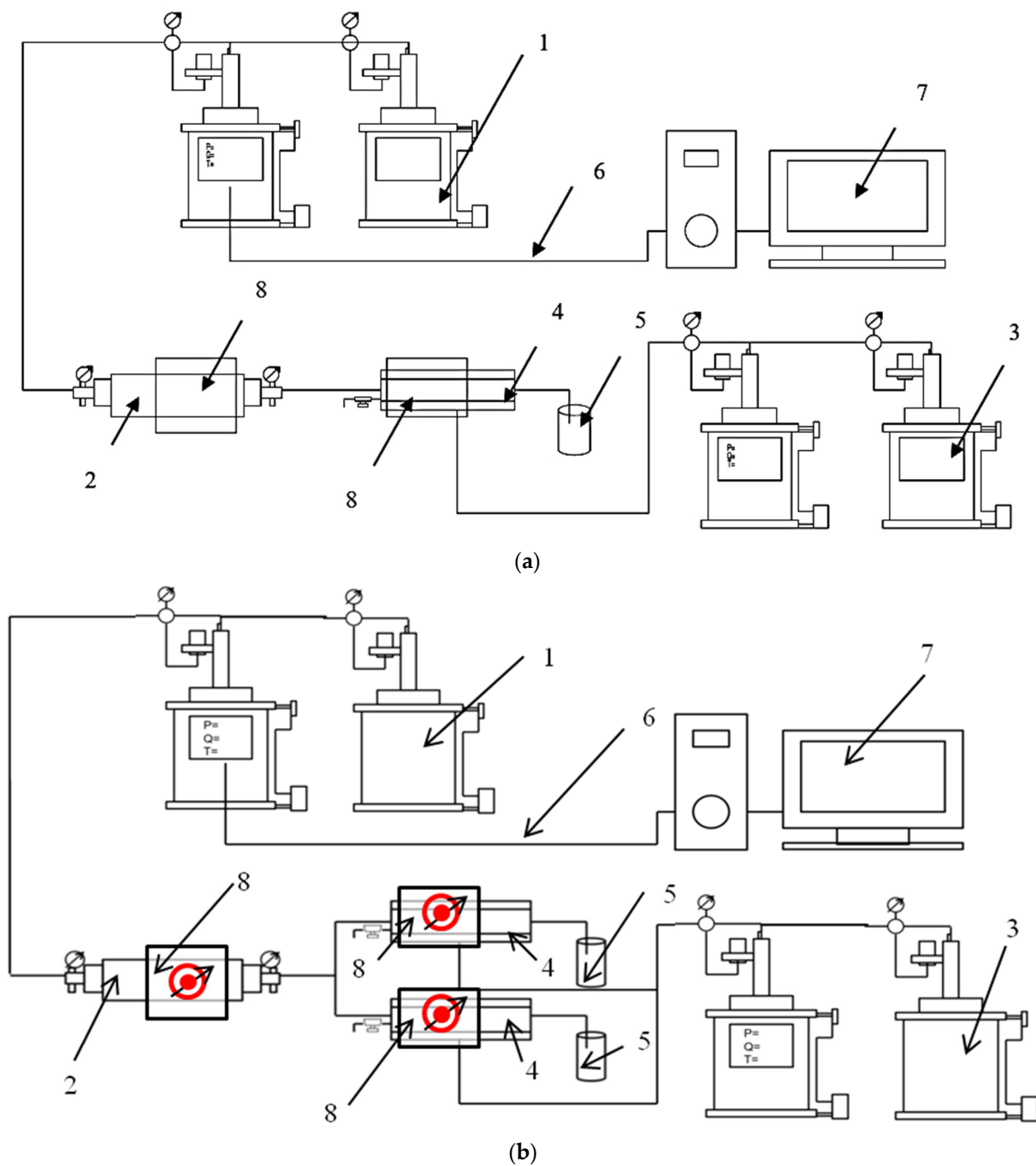
Figure 4. Schematic diagram of the core flooding test with a single core model (**a**) and the core flooding unit for the testing conditions in the heterogeneous reservoirs (**b**). 1—injection pump; 2—sampler; 3—clamping system; 4—core holders; 5—measuring containers; 6—tubes and fittings made of Hastelloy; 7—computer with a program for recording and adjusting the pump operation parameters; 8—heated casing for the sampler and the core holder.

The core flooding experiment included the following stages:

- Likewise, before the main part of the test, residual water saturation and residual oil saturation were designed. At this stage, the oil volume that was the saturated cores was fixed (V_{io});
- Then, the model of the reservoir water was injected into the parallel core unit before a 100% water cut was reached. At this stage, which was called the water injecting stage, there were estimated: the displacement coefficient (*DC*) before treatment, the

effective permeability of water, volume of displaced oil (V_{dow1}), and the amount of water through each core;

- In the follow-up step, the polymer composition was injected at a constant flow rate ($Q = 0.5$ mL/min) in the amount of 1 *PV*. The volume of displaced oil (V_{dop}) was measured. The flooding test was carried out in the "forward" direction. This stage was called the gelant injecting stage;

- Previously, there was injected the alkaline solution at a constant flow rate ($Q = 0.5$ mL/min) in the amount of 1 *PV* into the core samples No. 1A and 1B. The effective permeability of the alkaline solution was measured. The flooding was carried out in the "forward" direction;

- Once the polymer composition was injected, the core samples were aged for 24 h;

- Then, the water was injected into the simulated reservoir, in order to define the oil displacement coefficient after the treatment. The volume of the displaced oil was also measured for each sample (V_{dow2}). The flooding test was carried out in the "forward" direction;

- The next step was to estimate the selectivity coefficient (*SC*). *SC* represents which zone (oil- or water-saturated) of the formation is plugged by the polymer composition. The polymer composition with a higher selectivity coefficient has penetrated less into the water-saturated zones. The next equation was used to define the selectivity coefficient:

$$SC = \frac{V_{\text{w}}}{V_{\text{t}}}, \tag{6}$$

where:

V_{w}—volume of water, that was flooded into the high-permeable sample, mL;
V_{t}—the total volume of water, that was injected into the simulated reservoir, mL.

4. Results and Discussion

In this part of the paper, the results of the laboratory studies obtained for the initial and proposed polymer compositions were compared.

4.1. Absorption Spectra Study: Results

The Raman spectra of the polymer compositions are shown in Figure 5. Taking into account the obtained spectra and the literature sources, the following possible bonds can be highlighted in the decreasing order of the absorption wavenumber: free stretching vibrations of the OH bonds, bound stretching O-H, valence C-H, valence H-C-H, valence C-O-O-, planar deformation vibrations O-H, deformation H-C-H, valence C-O, scissor vibrations C-O-O-, valence C-C, out-of-plane vibrations O-H, rocking vibrations H-C-H, deformation C-H, and wagging deformation vibrations C-O-O- [23].

The oscillations of the bonds in the compounds of the O-Cr-O type are usually observed in the fingerprint area (500–200 cm^{-1}). In this area, the obtained spectra show a high concentration of peaks, which makes it impossible to interpret and establish the type of connection.

The vibrations of the C≡N bond characteristic of HPAN are observed at wavenumbers 2260–2240 cm^{-1}. An increase in the intensity of both stretching and the scissor deformation and wagging deformation vibrations of the carboxylate anion in the proposed polymer composition is observed.
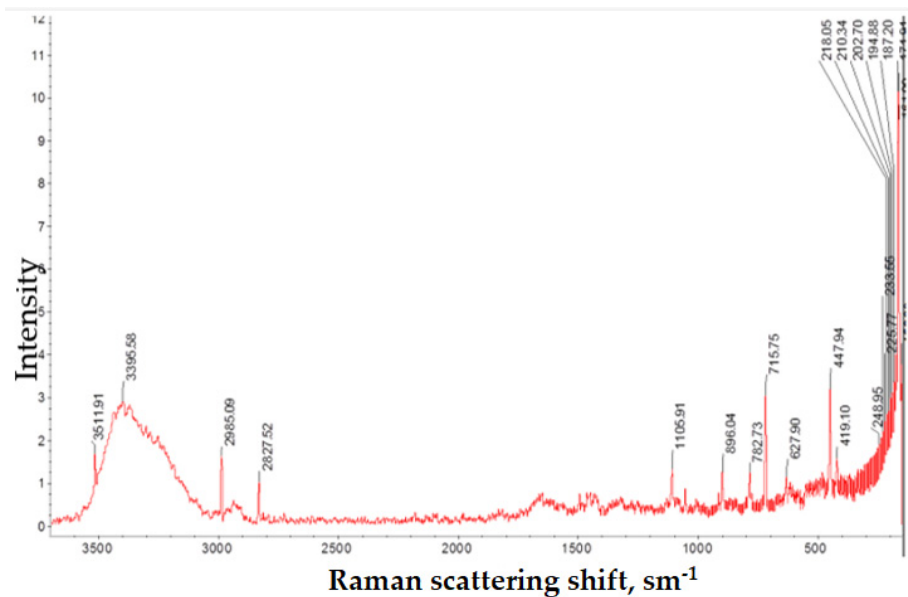
The addition of a gel-time modifier and neutralizer (HCl and NaOH) led to an increase in the concentration of the COO- groups, which are capable of forming O-Al-O, O-Cr-O or O-Fe-O bridges with polyvalent metal cations.

4.2. Hydrogen Index Study: Results

The results of determining the pH of the proposed polymer composition are presented in Table 1.
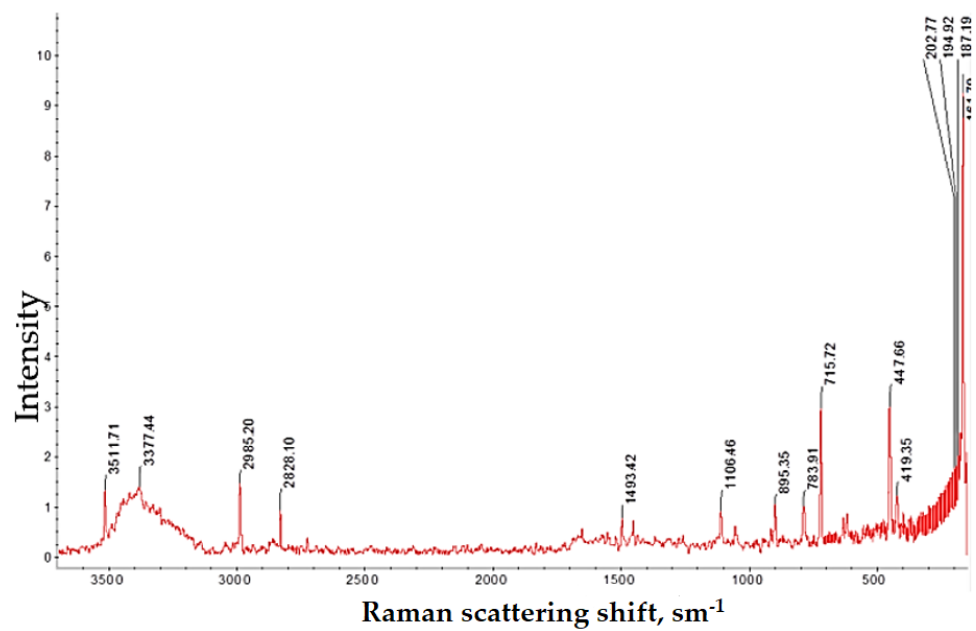
(**a**)

(**b**)

Figure 5. Raman spectra of the compounds formed in the polymer composition without a gelation gel-time modifier (**a**) and in the developed polymer composition (**b**).

Table 1. PH values at the different contents of the gelation delayer and neutralizer components.

No.	Concentration of 12% Solution HCl C_{HCl} (%)	Solution pH	Concentration of 10% Solution NaOH C_{NaOH} (%)	Solution pH
1	0.2300	3.57	0.3424	7.58
2	0.4900	3.34	0.6848	7.58
3	1.0090	3.13	1.4038	7.30
4	2.0121	2.96	2.8280	7.75
5	3.0120	2.84	4.2160	7.44
6	4.0067	2.78	5.6125	7.35
7	5.0056	2.72	7.0163	7.57

The power law between the pH of the polymer solution and the content of the gelation delayer was established. The concentrations of the neutralizer were selected, in order to adjust the pH of the polymer composition to neutral. This condition satisfies the requirement of a water plugging barrier forming in the reservoir. It should also be noticed that the dependence between the alkali content of the polymer composition, which is sufficient for neutralization, and the concentration of hydrochloric acid is linear.

4.3. Plastic Strength Study: Results

The polymer composition, based on HPAN and crosslinked with a chromium acetate solution, acquires a high strength at a polymer content of only 3% or more (Table 2).

Table 2. Results of determining the plastic strength and gelation time of the polymer composition, based on the HPAN and chromium acetate.

No.	Polymer Concentration C_{pol}, %	Crosslinker Concentration C_{crsl}, % (Chromium Acetate)	Gelation Time, min.	Plastic Strength, Pa		
				After 24 h	After 48 h	After 72 h
1	0.5	0.1	Did not crosslink (thickened composition)	Not strong	Not strong	Not strong
2	1	0.1	Did not crosslink (thickened composition)	Not strong	Not strong	Not strong
3	2	0.2	Did not crosslink (thickened composition)	Not strong	Not strong	Not strong
4	3	0.3	1140	Not strong	343.60	1747
5	4	0.4	150	5049	5796	5796
6	5	0.5	105	6722	5796	5796

We carried out studies to assess the effect of the gel-time modifier on the strength of the polymer composition. A strong polymer gel with a polymer content $C_{pol} = 4\%$ and a crosslinker $C_{crsl} = 0.4\%$ was selected as the initial water plugging composition. The results are shown in Table 3.

Table 3. Results of finding the plastic strength and the gelation time with the addition of a gelation delayer and a neutralizer to the polymer solution, based on the HPAN and chromium acetate.

No.	Concentration of 12% Solution C_{HCl}, %	Concentration of 10% Solution C_{NaOH}, %	Gelation Time, min	Plastic Strength, Pa		
				After 24 h	After 48 h	After 72 h
1	0.25	0.34	24	4438	5049	5796
2	0.5	0.68	24	5403	6233	6233
3	1	1.40	28	5796	6722	6722
4	2	2.83	26	6233	8590	8590
5	3	4.22	28	9389	9389	9389
6	4	5.61	23	8590	8590	10,304
7	5	7.02	26	3931	7889	9389
8	6	8.42	20	3709	7270	7270

To assess the nature of the change in the plastic strength of the polymer composition (crosslinker—$Cr(CH_3COO)_3$), with different contents of the gelation delayer and neutralizer, the graphs of the dependences of these parameters were plotted after 24 h (Figure 6).

The maximum P_s is reached at $C_{HCl} = 3$–4% and $C_{NaOH} = 4.22$–5.61%. Then, after 24 h, the plastic strength of the proposed polymer composition (crosslinker—$Cr(CH_3COO)_3$) increased by 1.7 times, compared to the original composition.

4.4. Rheological Study: Results

The selection of the gel-time modifier components' optimal concentrations (the gelation delayer, HCl, and the neutralizer, NaOH) was based on estimating the effective viscosity of the polymer compositions over time. Initially, the effective viscosity of the polymer composition with different HCl contents was found, and then the amount of NaOH sufficient for the neutralization was found.
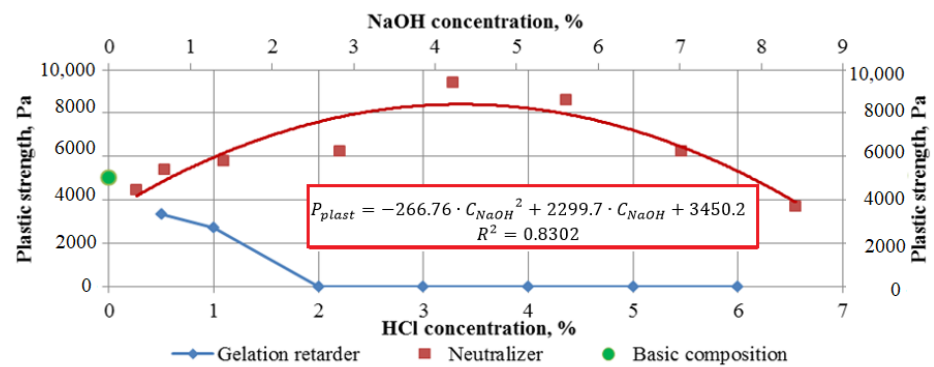
Figure 6. The dependence between the plastic strength (P_s) and the concentrations of the gelation delayer (C_{HCl}), and neutralizer (C_{NaOH}) after 24 h, from the time of crosslinking (crosslinker—Cr(CH$_3$COO)$_3$). The green point indicates the composition without the gel-time modifier (basic composition).

The polymer compositions with HCl (12% solution) less than 2% (1st group, Figure 7 on the left), demonstrated a sharp increase in the effective viscosity (μ_{eff}), up to 4000–4500 mPa·s over 12–40 min, which is equal to the period of the polymer gelation by the chromium cations. The extremum that determines the polymer gel system crosslinking time was not observed with more than 3% of HCl (12% solution). The effective viscosity decreased by 2–2.5 times and stabilized at the given values (2nd group, Figure 7 on the right), which confirms the theoretically substantiated ideas for selecting the components of the gel-time modifier. Adding 4%, 5%, and 6% HCl, reduced the effective viscosity to approximately equal levels.
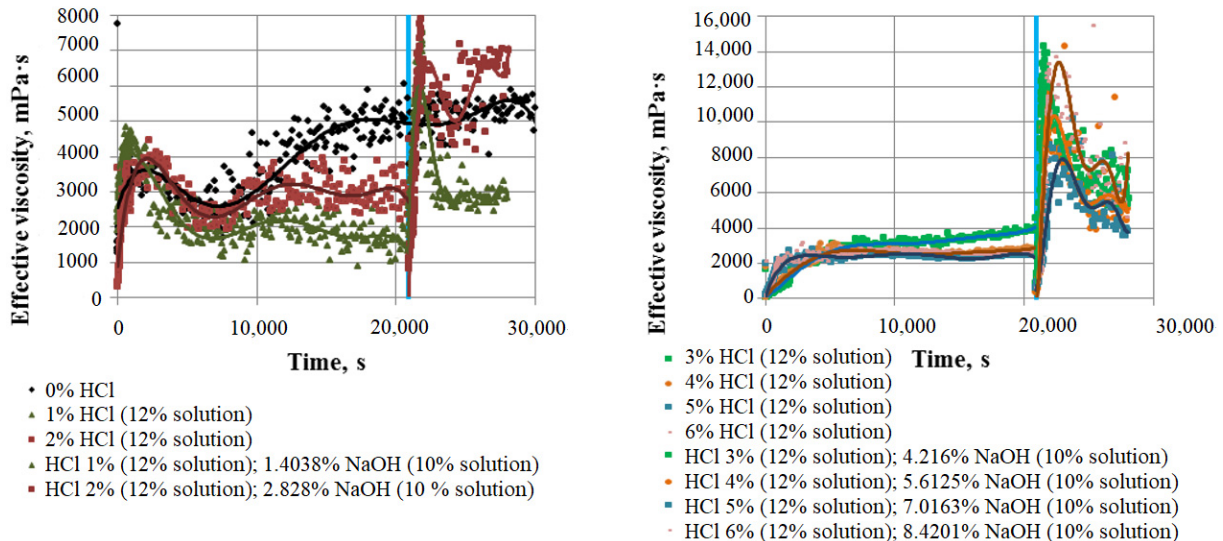

- 0% HCl
- 1% HCl (12% solution)
- 2% HCl (12% solution)
- HCl 1% (12% solution); 1.4038% NaOH (10% solution)
- HCl 2% (12% solution); 2.828% NaOH (10 % solution)

- 3% HCl (12% solution)
- 4% HCl (12% solution)
- 5% HCl (12% solution)
- 6% HCl (12% solution)
- HCl 3% (12% solution); 4.216% NaOH (10% solution)
- HCl 4% (12% solution); 5.6125% NaOH (10% solution)
- HCl 5% (12% solution); 7.0163% NaOH (10% solution)
- HCl 6% (12% solution); 8.4201% NaOH (10% solution)

Figure 7. The dependence between the effective viscosity of the polymer composition (HPAN 4%, Cr(CH$_3$COO)3 0.4%) and the concentration of the gelation delayer and neutralizer over time. The blue line indicates the moment of adding NaOH.

The addition of the neutralizer doubles the effective viscosity, while a sharp increase in the last one indicates the elongation of the coiled molecules and the crosslinking of the polymer (Figure 7).

Table 4 shows the generalized results of determining the effective viscosity of the polymer compositions with the components of the gel-time modifier and the initial composition.

At the same polymer and crosslinker contents, the proposed polymer composition has an effective viscosity that is 2 to 2.5 times lower than the initial one (without the gel-

time modifier). In the conditions of the oil reservoir, where it contacts with the alkali, the effective viscosity increases by 2–3 times, relative to the initial composition.

Table 4. The effective viscosity of the initial and proposed compositions with different contents of the gel-time modifier: HCl and NaOH (12% HCl solution).

No.	Time, min.	Effective Viscosity, mPas						
		HCl content, % of weight						
		0% (Initial)	1%	2%	3%	4%	5%	6%
1	10	3770	3940	2600	340	555	1080	
2	60	3310	1740	3920	2130	2110	2800	2640
3	120	2360	1760	2030	3130	2500	2520	2580
4	300	5900	1600	2910	3420	2620	2390	2540
		NaOH content, % of weight						
		0% (Initial)	1.4038%	2.828%	4.216%	5.6125%	7.0163%	8.4201%
5	10	3770	6710	6120	13,100	7290	2800	5450
6	60	3310	2830	4980	8210	6480	8880	8600
7	120	2360	2820	7010	5680	5110	3850	5500

4.5. Corrosion Rate Study: Results

The proposed polymer composition has a low corrosivity. The corrosion rate values do not exceed the standards of 0.1–0.12 mm/year, established for killing fluids in GOST 9.506-87 (Table 5).

Table 5. The corrosion rate of polymer compositions.

No.	Temperature, °C	Corrosion Rate, mm/Year	
		(Initial)	(Proposed)
1	20	0.0611	0.0627
2	105	0.0962	0.0973

Despite the presence of a gelation delayer (HCl, which is a corrosive substance) in the polymer composition, the corrosion rate does not exceed the established standards for process fluids due to the neutralization of the Cl^- anions on the metal surface (previously kept in a NaOH solution) by the alkali with the formation of the NaCl salt.

4.6. Degradation Study: Results

The results of the polymer gel-degrading fluid selection for the polymer composition (HPAN (4%) + (CH3COO)3Cr (0.4%) + HCl (1.7%) + NaOH (6%) + H_2O (remaining)) are presented in Table 6.

Table 6. Results of the selection of a destructing agent for the polymer composition with a gel-time modifier.

No.	Gel-degrading Fluid Name	Polymer Mass Before, g	Polymer Mass After, g	Relative Mass Change, %
1	H_2O	4.787	15.383	321.3
2	HCl (12% solution)	4.818	3.617	75.1
3	HNO_3 (12% solution)	4.873	6.396	131.3
4	CH_3COOH (12% solution)	5.007	6.464	129.1
5	HCOOH (12% solution)	4.740	6.160	130.0

The greatest degradation of the proposed polymer composition occurred when a 12% solution of HCl was added. In other cases, the polymer started swelling, as evidenced by

an increase in the mass after the experiment. Thus, as a destructing agent for the polymer composition, hydrochloric acid can be used, which causes the greatest degradation (25%).

4.7. Plugging the Efficency Evaluation through the Core Flooding Tests: Results

4.7.1. Single Core Model Test: Results

The results of the investigation and the estimation of the injection gradient pressure (*gradP*) of the initial polymer composition and the proposed one with the gel-time modifier after injecting 1 *PV*, the initial shear pressure gradient (*gradP*$_s$), the resistance factor (*RF*), the residual resistance factor (*RRF*), and other characteristics that were mentioned in part 2.7.1, were presented in Tables 7 and 8.

Table 7. Results of the core flooding tests at a single core model of the proposed polymer composition without a gel-time modifier.

No.	Sample Number	K_{abs}, 10^{-3} μm²	*m*, %	*gradP* at 1 *PV* MPa/m	*gradP*$_s$, MPa/m	*RRF*	*RF*
1	1	18.5	27	0.03	1.17	87	90
2	2	20	29	2.19	2.19	182	182
3	3	30	30	0.12	0.85	198	198
4	7	1.25	26	2.3	2.81	15	15
5	8	8.11	29	2.57	2.58	87	87

Table 8. Results of the core flooding tests at a single core model of the proposed polymer composition with a gel-time modifier.

No.	Sample Number	K_{abs}, 10^{-3} μm²	*m*, %	*gradP* at 1 *PV* MPa/m	*gradP*$_s$, MPa/m	*RRF*	*RF*
1	4	16.8	30	0.072	1.93	136	136
2	10	17.6	27	0.6	2.24	165	166
3	14	19.34	30	0.98	2.24	182	182
4	9	31	31	0.0118	2.15	285	286
5	13	6.65	28	0.023	2.24	62	63

The results of studying the penetrating characteristics of the proposed polymer composition confirmed its superiority over the original polymer composition without a gel-time modifier. The pressure gradients of the polymer solution with a gel-time modifier after injecting one pore volume, are substantially lower than the pressure gradient of the initial. At the same time, the shear pressure gradient and the residual resistance factor are higher, due to a better conformance of the water-saturated area with the proposed polymer composition.

4.7.2. Parallel Core Model Test: Results

The results of determining the displacement coefficients (*DCs*) of oil before and after treatment, the selectivity (*SC*), amount of water flow in each core in % (*WF*), the volume of displaced oil on each stage (V_{dow1}, V_{dop}, V_{dow2}) are presented in Tables 9 and 10.

Table 9. Examination of the polymer composition without a gel-time modifier.

No.	Sample Number	*m*, %	V_{io}, mL	K_{abs}, 10^{-3} μm²		Water Injection Stage		Gelant Injection Stage	Post Water Injection Stage		DC Before Treatment	DC After Treatment
						WF, %	V_{dow1}, mL	V_{dop}, mL	*WF*, %	V_{dow2}, mL		
1	High-permeability sample 2C	33	7.9	30.3		100	4.8	1.8	0	0	0.61	0.23
2	Low-Permeability sample 2D	31	6.3	0.99		0	0	1.8	0	0	0	0.29
3	Entire model		14.2	Before treatment 24	After treatment 0.1		4.8	3.6		0	0.34	0.25

Table 10. Examination of the polymer composition with a gel-time modifier.

No.	Sample Number	m, %	V_{io}, mL	K_{abs}, 10^{-3} μm²	Water Injection Stage		Gelant Injection Stage V_{dop}, mL	Post Water Injection Stage		*DC* Before Treatment	*DC* After Treatment	*SC*
					WF, %	V_{dow1}, mL		*WF*, %	V_{dow2}, mL			
1	High-permeability sample 1A	31	6.6	3.7	100	5.6	0.6	21	0	0.85	0.09	0.21
2	Low-permeability sample 2B	28	6.8	1.1	0	0.4	3.2	79	0.4	0.06	0.59	0.79
3	Entire model		13.4			6	3.8		0.4	0.45	0.34	

It should be noted that the displaced oil volume was estimated by capillary viscosimetry to separate oil and water from the total volume of the displaced fluid.

Figure 8a depicts three zones of the flooding process: the water injection stage, gel placement stage, and post-flooding one. The first stage had a low resulted pressure gradient, due to the water direction only into the high-permeability sample (*WF* = 100%). So, the oil was displaced by water only from the sample No. 2C and amounted to 4.8 mL.
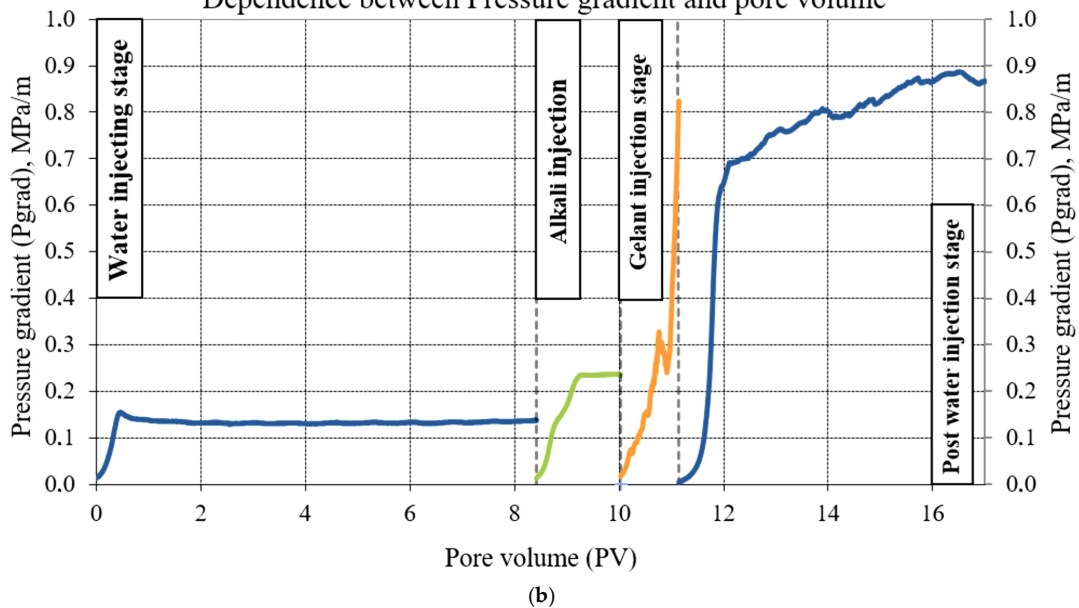

(a)

(b)
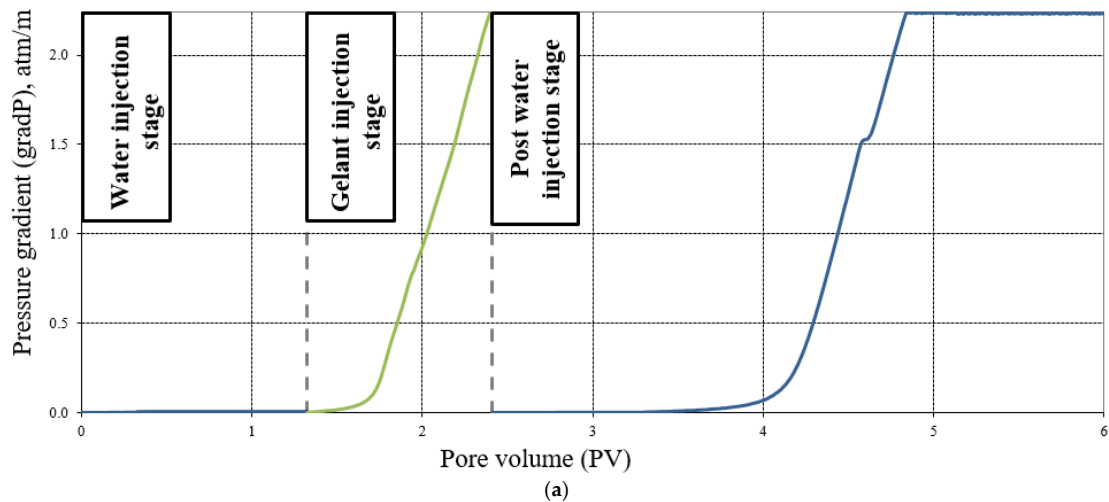
Figure 8. Injection curve during the experiment for the initial composition (**a**) and the proposed one (**b**).

During the polymer composition injection into the heterogeneous reservoir model, the oil was displaced from the high-permeable as well as the low-permeable core samples, which exemplifies the penetration of the gelant into both cores, due to its high viscosity. This was demonstrated during the gelant injection stage. The pressure gradient increased steadily during the gelant injection.

The third stage of the experiment showed a continuous rise in the pressure gradient, but finally, after 4.8 *PV*, it started to level off and had reached 2.2 MPa/m. The plateau was observed because of a safety pressure of a pump reaching its limit.

Following the polymer composition injection, it was observed that water had been injected neither in high-permeable nor in low-permeable samples. Thus, the polymer composition penetrated and plugged the oil-saturated area. In this regard, it was impossible to estimate the selectivity coefficient.

The injection of the proposed polymer composition led to an increase in the displacement coefficient of 20%, compared with the effect of the original composition without a gel-time modifier. At the same time, the water cut decreased by 4%. The positive effect was obtained due to the creation of a durable water barrier (strong gel) in the water-saturated zone. It was noticed, that 79% of the injected water moved into the oil-saturated sample and only 21% moved through the water-saturated one. Thus, the proposed composition is highly selective in relation to the water saturation zones.

Figure 8b depicts four stages of the flooding process: the water injection, the alkali injection, the gel placement, and the post flooding one. The pressure gradient increased sharply to 0.145 MPa/m and then remained constant at 0.133 MPa/m at the first stage. Then, the alkali solution was injected, so the pressure gradient demonstrated the same dynamic as in the first stage. It was levelled off at 0.241 MPa/m. The gradient pressure on the gelant injection stage demonstrated wild fluctuations, but in general the trend was upward. The gradient pressure on the final stage of the experiment showed the sharp rise at the first period of the stage, but then it presented slight fluctuations.

It was found that the injection curve of the polymer composition with a gel-time modifier was characterized by some peaks. Hence, there was the neutralization of hydrochloric acid and the polymer crosslinking. This feature can be used as a benchmark in carrying out operations for the conformance improvement.

5. Conclusions

In this study, the experiments are performed to determine and compare the physical and chemical characteristics of the developed polymer compositions, with and without a gel-time modifier, for the conformance control in heterogeneous reservoirs. The component composition and concentration levels of the gelation delayer and neutralizer were selected, based on alterations in the hydrogen index of the polymer solution. This approach to the gel-time modifier component selection made it possible to create a water plugging composition with improved physicochemical and rheological properties, in comparison with the initial polymer composition.

The proposed polymer composition has good technological properties, such as a low initial viscosity, high plastic strength, corrosion resistance, good penetration, and good water plugging ability. As a result of the polymer gel treatment, the water cut decreased by 4%, and the displacement coefficient of the oil increased by 20%, in comparison with the effect of the original composition without a gel-time modifier.

The obtained properties of the polymer composition with the gel-time modifier allow it to be recommended for re-treatments as well. The field application is recommended to confirm the effects obtained under laboratory conditions.

The authors filed a patent application for their invention, based on the research findings. The patent application number is 2022125245 (RU).

References

1. Averyanova, O.Y. Domanik type petroleum systems in Timan-Pechora sedimentary basin. *Neftegazov. Geol. Teor. I Prakt.* **2016**, *11*, 1–30. [CrossRef]
2. Buslaev, G.; Tsvetkov, P.; Lavrik, A.; Kunshin, A.; Loseva, E.; Sidorov, D. Ensuring the Sustainability of Arctic Industrial Facilities under Conditions of Global Climate Change. *Resources* **2021**, *10*, 128. [CrossRef]
3. Loseva, E.; Lozovsky, I.; Zhostkov, R.; Syasko, V. Wavelet Analysis for Evaluating the Length of Precast Spliced Piles Using Low Strain Integrity Testing. *Appl. Sci.* **2022**, *12*, 10901. [CrossRef]
4. Gizatullin, R.R.; Budovskaya, M.E.; Dvoynikov, M.V. Development of Detergent for Drilling Muds While Directional Drilling. In *Advances in Raw Material Industries for Sustainable Development Goals*; CRC Press: London, UK, 2020; pp. 309–313.
5. Prishepa, O.M.; Nefedov, Y.V.; Kochineva, O.E. Raw material base of hard-to-extract oil reserves of Russia. *Periódico Tchê Química* **2020**, *17*, 915–924. [CrossRef]
6. Filimonova, I.V.; Nemov, V.Y.; Prompt, I.V.; Mishenin, M.V.; Komarova, A.V.; Zemnukhova, E.A.; Shumilova, S.I.; Kozhevin, V.D.; Nikiforenko, E.K.-M.; Kontorovich, A.E. Oil industry-2020: Long-term trends and current state. In *Oil and Gas Complex of Russia*; Publishing House of INGG SB RAS: Novosibirsk, Russia, 2021; p. 88. ISBN 978-5-4437-1222-2, 978-5-4437-1221-5.
7. Palyanitsina, A.; Safiullina, E.; Byazrov, R.; Podoprigora, D.; Alekseenko, A. Environmentally Safe Technology to Increase Efficiency of High-Viscosity Oil Production for the Objects with Advanced Water Cut. *Energies* **2022**, *15*, 753. [CrossRef]
8. Zhu, D.; Bai, B.; Hou, J. Polymer Gel Systems for Water Management in High-Temperature Petroleum Reservoirs: A Chemical Review. *Energy Fuels* **2017**, *31*, 13063–13087. [CrossRef]
9. Shagiakhmetov, A.; Yushchenko, S. Substantiation of In Situ Water Shut-Off Technology in Carbonate Oil Reservoirs. *Energies* **2022**, *15*, 5059. [CrossRef]
10. Mardashov, D.V.; Limanov, M.N. Improving the efficiency of oil well killing at the fields of the volga-ural oil and gas province with abnormally low reservoir pressure. *Bull. Tomsk. Polytech. Univ. Geo Assets Eng.* **2022**, *333*, 185–194. [CrossRef]
11. Islamov, S.R.; Bondarenko, A.V.; Gabibov, A.F.; Mardashov, D.V. Polymer compositions for well killing operation in fractured reservoirs. In *Advances in Raw Material Industries for Sustainable Development Goals*; CRC Press: London, UK, 2020; pp. 343–351.
12. Rogachev, M.K.; Mukhametshin, V.V.; Kuleshova, L.S. Improving the efficiency of using resource base of liquid hydrocarbons in Jurassic deposits of Western Siberia. *J. Min. Inst.* **2019**, *240*, 711–715. [CrossRef]
13. Leusheva, E.; Morenov, V.; Liu, T. Dependence of the Equivalent Circulation Density of Formate Drilling Fluids on the Molecular Mass of the Polymer Reagent. *Energies* **2021**, *14*, 7639. [CrossRef]
14. Mardashov, D. Development of blocking compositions with a bridging agent for oil well killing in conditions of abnormally low formation pressure and carbonate reservoir rocks. *J. Min. Inst.* **2021**, *251*, 617–626. [CrossRef]
15. Rellegadla, S.; Prajapat, G.; Agrawal, A. Polymers for enhanced oil recovery: Fundamentals and selection criteria. *Appl. Microbiol. Biotechnol.* **2017**, *101*, 4387–4402. [CrossRef] [PubMed]
16. Zhao, H.; Zhao, P.; Bai, B.; Xiao, L.; Liu, L. Using Associated Polymer Gels to Control Conformance for High Temperature and High Salinity Reservoirs. *J. Can. Pet. Technol.* **2006**, *45*, 49–54. [CrossRef]
17. Krevelen, D.W.V. *Properties of polymers: Their Correlation with Chemical Structure, Their Numerical Estimation and Prediction from Additive Group Contributions*; Elsevier: New York, NY, USA, 1997; ISBN 044482877X.
18. Procedure for Treatment of Underground Reservoir Using Rheological Model for Optimisation of Fluid Medium. Available online: https://www.fips.ru/cdfi/fips.dll/ru?ty=29&docid=2424428 (accessed on 11 July 2022).
19. Method for Water Inflow Isolation in High-Temperature Reservoirs. Available online: https://patents.s3.yandex.net/RU2272891C1_20060327.pdf (accessed on 11 July 2022).
20. Sydansk, R.D. Polymers, Gels, Foams and Resins. In *Petroleum Engineering Handbook*; Society of Petroleum Engineers: Houston, TX, USA, 2007; pp. 1219–1224. ISBN 978-1-55563-120-8.
21. Ghosh, P.; Metidji, M.O.; Dupuis, G.; Wilton, R.; Ravikiran, R.; Bowers, A.; Seright, R. Pushing the Envelope of Polymer Injectivity in Low Permeability Sandstones. In Proceedings of the IOR 2021–21st European Symposium on Improved Oil Recovery; EAGE, Online Event, 19–22 April 2021; p. 21.
22. Bershtein, V.A.; Ryzhov, V.A. Far infrared spectroscopy of polymers. In *Polymer Analysis and Characterization*; Springer: Berlin/Heidelberg, Germany, 1994; pp. 43–121.

23. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*; John Wiley & Sons: New York, NY, USA, 2009; ISBN 978-0-471-74493-1.

24. Mardashov, D.; Duryagin, V.; Islamov, S. Technology for Improving the Efficiency of Fractured Reservoir Development Using Gel-Forming Compositions. *Energies* **2021**, *14*, 8254. [CrossRef]

25. Sultanbekov, R.R.; Terekhin, R.D.; Nazarova, M.N. Stress-stain state of a vertical steel tank affected by bottom sediments inconditions of extreme temperature differences. In *Advances in Raw Material Industries for Sustainable Development Goals*; Taylor & Francis: London, UK, 2021.

26. Martyushev, D.A.; Govindarajan, S.K. Development and study of a visco-elastic gel with controlled destruction times for killing oil wells. *J. King Saud Univ.-Eng. Sci.* **2021**, *34*, 408–415. [CrossRef]