

Article

Development of Selective Acidizing Technology for an Oil Field in the Zechstein Main Dolomite

Marek Czupski ^{1,*} , Piotr Kasza ¹  and Łukasz Leśniak ²¹ Oil and Gas Institute—National Research Institute, 25A Lubicz str., 31-503 Krakow, Poland; kasza@inig.pl² Brenntag Polska, Jana Bema 21 str., 47-224 Kędzierzyn Koźle, Poland; lukasz.lesniak@brenntag-cee.com

* Correspondence: czupski@inig.pl

Received: 28 September 2020; Accepted: 12 November 2020; Published: 13 November 2020



Abstract: This paper presents laboratory studies based on which a stimulation technology for an oil field located in the Zechstein Main Dolomite was investigated. A large number of oil wells in the Main Dolomite produce significant amounts of reservoir water. Matrix acidizing using conventional acid solutions in such wells has caused a significant increase in water cut, because of their affinity for water. The purpose of this cooperation between the Oil and Gas Institute–NRI and the Brenntag Polska was to develop an acid treatment technology that would not increase the water cut after acidizing treatment in wells where oil production is accompanied by the production of reservoir water. Therefore, a series of tests were performed, including the selection of a suitable viscoelastic surfactant that was sensitive to crude oil. The contact of the gel of the viscoelastic surfactant fluid with crude oil resulted in the reduction of its viscosity. The tests described herein include dissolution/dispersion tests, rheological tests, acid sludge tests, compatibility tests, core flow experiments, and corrosion tests, which allowed recipes to be developed for the preflush, diverter, and acidizing liquid. Then, recommendations were established for using these liquids in matrix acid treatment. A series of treatments performed according to this technology allowed the removal of near-wellbore damage without increasing the water cut.

Keywords: matrix acidizing; viscoelastic surfactant; fluid composition; dolomite formation

1. Introduction

The purpose of matrix acidizing treatment of carbonate formations is to increase production from the well. This treatment is carried out by creating channels, called wormholes, with high permeability in the near-wellbore area. These channels form because of the natural heterogeneity of permeability of the rock matrix, which leads to differences in the flow of acidizing fluids in each of its elements. In areas where the flow rate is higher, greater dissolution of the matrix occurs, which causes an additional increase in flow in these zones. During preparation of the acidizing treatment of carbonate formations, special attention should be paid to the fast reaction rate of the reservoir rock and acid at an elevated temperature, contrast of formation permeability in the interval to be treated, and the possible occurrence of zones with high water saturation. To retard the acid-rock reaction rate and increase the acid consumption time, the following techniques are applied [1,2]: the use of stronger acid solutions, resulting in higher amounts of acid available for the reaction, and consequently in the release of higher concentrations of products (CaCl_2 , MgCl_2 and CO_2), which further retards the reaction; addition of chemical retarders to acid solutions, which form protective films on the surfaces of carbonate rock; the use of foamed acid, which is particularly effective for stimulating low-permeability carbonate formations; the use of gelled acid based on polymers such as polyacrylamide [3] and surfactants such as those of the betaine group [4]; the use of organic acids, such as acetic acid, formic acid [5,6], and citric acid [7], chelate compounds such as EDTA [8,9] and GLDA [10], or mixtures of organic acids and

hydrochloric acid [11–13]; and the use of acid emulsions, including both micro-emulsions and coarse emulsions [14].

The following techniques are applied to retard the reaction rate. The polymers used in acidizing treatment must be chemically stable and increase the viscosity of the acidizing fluid. The retardation of chemical reaction is achieved by: reducing hydrogen ion contact with the carbonate rock surface by maintaining laminar flow, developing a film of gelling agent on the rock surface to inhibit direct acid contact, forming a filter cake under leakoff conditions [1]. In addition, gelled acids help remove insoluble fines after the treatment. In turn, cross-linked gelled acids characterized by almost two times slower reaction rate with calcite compared to gelled HCl with the same HCl concentration. The reason for this is the formation of a gel layer on the rock surface which decreased the acid diffusion rate to the solid surface [15]. Viscoelastic surfactant (betaine type) added to hydrochloric acid solution reduces the dissolution rate of calcite by reducing the diffusion coefficient of hydrogen ions [16]. Acid emulsions have the advantage, the most important of which are good thermal stability and their viscosity can be controlled by varying the ratio of oil to acid solution [17]. Emulsified acid systems can be divided into two types: microemulsions and coarse emulsions. In microemulsions, the droplets of acid are very small, much smaller than the rock pores, therefore the emulsion properties are maintained while the liquid is flowing through the pore space. In coarse emulsions the size of the acid droplets is usually larger than the pore size in the carbonate rock. The preparation costs of coarse emulsions are lower than microemulsions because only a small addition of emulsifier is required (typically less than 3%) while the volume of the acid solution phase, can be up to 80%. In microemulsions, the volume of the acid solution phase is limited to 30% with a large addition of emulsifying agent (even up to 20%) [14]. The tests showed low reaction rate of the emulsified acid systems (prepared at 15% HCl and 0.7 acid volume fraction) with dolomite at high temperature (110 °C). This reaction was limited by the rate of diffusion rate, which decreased with increasing the emulsifier concentration [18,19]. In turn, the use of a mixture of acetic and formic acids instead of hydrochloric acid solutions can minimize corrosion problems in high temperature formations [6]. The organic acids are used in mixtures containing hydrochloric acid, which has advantages over using each of these acids separately [11–13]. Organic acids are primarily used to increase the penetration of the active acid into the formation. Due to the low values of the dissociation constant, organic acids do not dissociate initially in a mixture with hydrochloric acid until HCl is almost completely spent. As the hydrogen ions from hydrochloric acid are depleted, this process begins for organic acids, resulting in further dissolution of the carbonate rock. In addition, formic acid is often used as a corrosion inhibitor intensifier at high temperatures. Their main disadvantages are: limited solubility of their calcium salts therefore cannot be used at high concentrations and the cost of dissolving a given weight of carbonate rock is significantly higher with organic acid than with hydrochloric acid [20]. The possibility of using methanesulfonic acid in acidizing treatment was also investigated, because it is a much stronger acid than the previously mentioned organic acids, so it dissociates completely in water [21]. It has also been noticed that chelates, e.g., ethylenediaminetetraacetic acid (EDTA), can be used as the main component of acidizing fluids [8,9]. Chelating agents compound L-glutamic acid, N,N-diacetic acid (GLDA) reacts with calcite and dolomite by two mechanisms depending on the pH of liquid. Proton attack is the dominant mechanism at low pH (<2), while at higher pH (>11) the main mechanism is the chelation mechanism [22]. GLDA has very good thermal stability and is also easily biodegradable.

In addition to retarding the reaction to allow for deeper penetration of the “active” acid into the formation, another requirement for the treatment fluid is ensuring contact of the entire stimulated interval with the acid [15]. For this purpose, diverters are used. Their task is to temporarily plug the zones with the highest permeability, such that the acidizing fluid can be diverted to other less permeable or more damaged zones. These agents can be divided into four main categories: ball sealers that degrade or dissolve in reservoir fluids or flowback to the surface after acidization, polymer gels, acid emulsions, foams, and fluids based on viscoelastic surfactants (VES).

The authors of this paper have focused on developing a system that uses VES. Some of these systems containing VES have low viscosities after preparation, usually below 50 cP, depending on the type and concentration of acid, the temperature, and the shear rate. During injection through the well into the reservoir formation, this type of fluid tends to flow primarily into the zones of the highest permeability, which require less stimulation. However, as the reaction of the acid with the carbonate rock progresses, calcium and/or magnesium ions are released, and the increase in fluid pH will increase the viscosity of the surfactant-based system. This occurs as a result of aggregation of surfactant micelles. In these zones, the flow resistance increases, and subsequent portions of acid are diverted to other zones of lower permeability, potentially the most in need of stimulation. As the acid is consumed, the fluid returns to its initial viscosity, or some salts such as NH_4Cl can be added to reduce the viscosity [23–30]. Systems that cause temporary blockage of water-bearing zones are also used in acidizing treatments in oil wells that produce significant amounts of reservoir water, so that oil-bearing zones are more effectively stimulated. Because micelles formed by viscoelastic surfactants are sensitive to hydrocarbons, fluids prepared on this basis can selectively block water saturated zones, whereas this effect will not occur in oil-saturated zones [31]. These types of properties, that is, the breakdown of the micelle network into smaller spherical micelles as a result of contact with hydrocarbons, are associated with anionic and betaine-group surfactants [4,32,33].

This paper presents part of the laboratory tests based on which stimulation technology for an oil field located in the Zechstein Main Dolomite was developed. The basic characteristics of this reservoir are presented in Table 1.

Table 1. Characteristic of the oil field in the Zechstein Main Dolomite.

Average reservoir temperature:	120 °C
Average permeability:	9–28 mD
Pressure:	38 MPa
Reservoir rock:	Dolomite (26–82%) Sulfates (10–20%) Anhydrite (10–30%)
Reservoir type:	Pore, fissure

At the beginning of the 21st century, matrix acidizing technology using acid emulsions was successfully applied in this oil field. The average increase in production was about 36% with a simultaneous drop in differential pressure [34]. This technology was developed because during the testing stage of the wells small scale acidizing treatment with solution of hydrochloric and acetic acid was not effective for stimulation of high temperature dolomite formation. At that time, some wells have also produced significant amounts of reservoir water. Treatments performed in such wells with the use of conventional acid solutions could have caused a significant increase in water cut. Therefore, the aim of this work was to implement technology that would increase oil production without a simultaneous increase in water production. When developing this technology, factors such as the compatibility of components, acid corrosion at high reservoir temperatures, thermal fluid stability and rheological properties, and possible formation of sludge and/or emulsion of treatment fluids with reservoir fluids should also be considered.

It is worth to emphasize, that the treatment liquids had to contain components that are approved in the European Union. This was a big challenge because many of the additives used in the global oil and gas industry cannot be applied in EU. It results from the European Parliament and Council Regulation (EC) No. 1907/2006 REACH concerning the use of chemicals, through their registration and evaluation and, in some cases, authorization and restriction on the marketing. So the chemical additives had to be approved for use in EU and effectively perform their functions. The selected

viscoelastic surfactant (VES) was sensitive to contact with crude oil and compared to e.g., polymers, the film that forms on the rock surface can be easily removed using mutual solvents.

2. Materials and Methods

2.1. Materials and Chemical Additives

Hydrochloric acid p.a. at a concentration of 36.5%, potassium chloride p.a., and calcium chloride hexahydrate p.a. were used in this research. Acid and salt solutions were prepared using tap water with electrical conductivity 540 $\mu\text{S}/\text{cm}$ at room temperature. The following agents were also used for the tests: three viscoelastic surfactants (TN-16234 amphoteric, and TN-16235 and TN-16237 anionic); three mutual solvents (TN-16300, the main component of which is a solvent belonging to the group of glycol ethers; TN-16305, the main component of which is butyl glycol, and TN-16310, the main component of which is another organic solvent); two microemulsions (TN-01700 mixture of chemical compounds based on propylene glycol and TN-01701 mixture based on isopropyl alcohol); a corrosion inhibitor (Brenntacor 6120LE, containing methanol, propargyl alcohol, pyridine, and alkyl derivatives); the corrosion inhibitor intensifier Brenntacor AID10 (inorganic iodine salt); and anti-sludge additives (TN-16640, a mixture based on isopropyl alcohol; TN-16650, a mixture of chemical compounds based on acetic acid; and TN-16660, a mixture of surfactants).

The compositions of crude oil and reservoir water used in the study are presented in Tables 2 and 3, respectively. In addition, organic sludge taken from one of the wells was used in the tests.

Table 2. Crude oil composition.

Density (g/cm^3)	Viscosity ($\text{mPa}\cdot\text{s}$)	Asphaltenes (%)	Resins (%)	Saturated Hydrocarbons (%)	Aromatic Hydrocarbons (%)
0.822	33.0	0.23	4.88	39.60	5.53

Table 3. Reservoir water properties and composition.

Density (at 22 °C) (g/cm^3):	1.214
pH:	5.89
Sodium concentration (mg/l):	107,001
Potassium concentration (mg/l):	6267
Calcium concentration (mg/l):	34,003
Magnesium concentration (mg/l):	2429
Chloride concentration (mg/l):	239,453
Bromide concentration (mg/l):	2128
Sulfates concentration (mg/l):	220
Bicarbonates concentration (mg/l):	275

Cylindrical core plugs with a diameter of 3.81 cm and a length of 4.2 cm were cut from a block of the Main Dolomite rock. Core plugs were then cleaned by extraction in a Soxhlet apparatus using a set of different solvents and dried at 115 °C until a constant weight was obtained. The permeabilities of the core plugs were 3.0 mD and 39.2 mD, and the porosities were 18.08% and 17.66%, respectively.

2.2. Methods

The adopted research concept is shown in Figure 1.

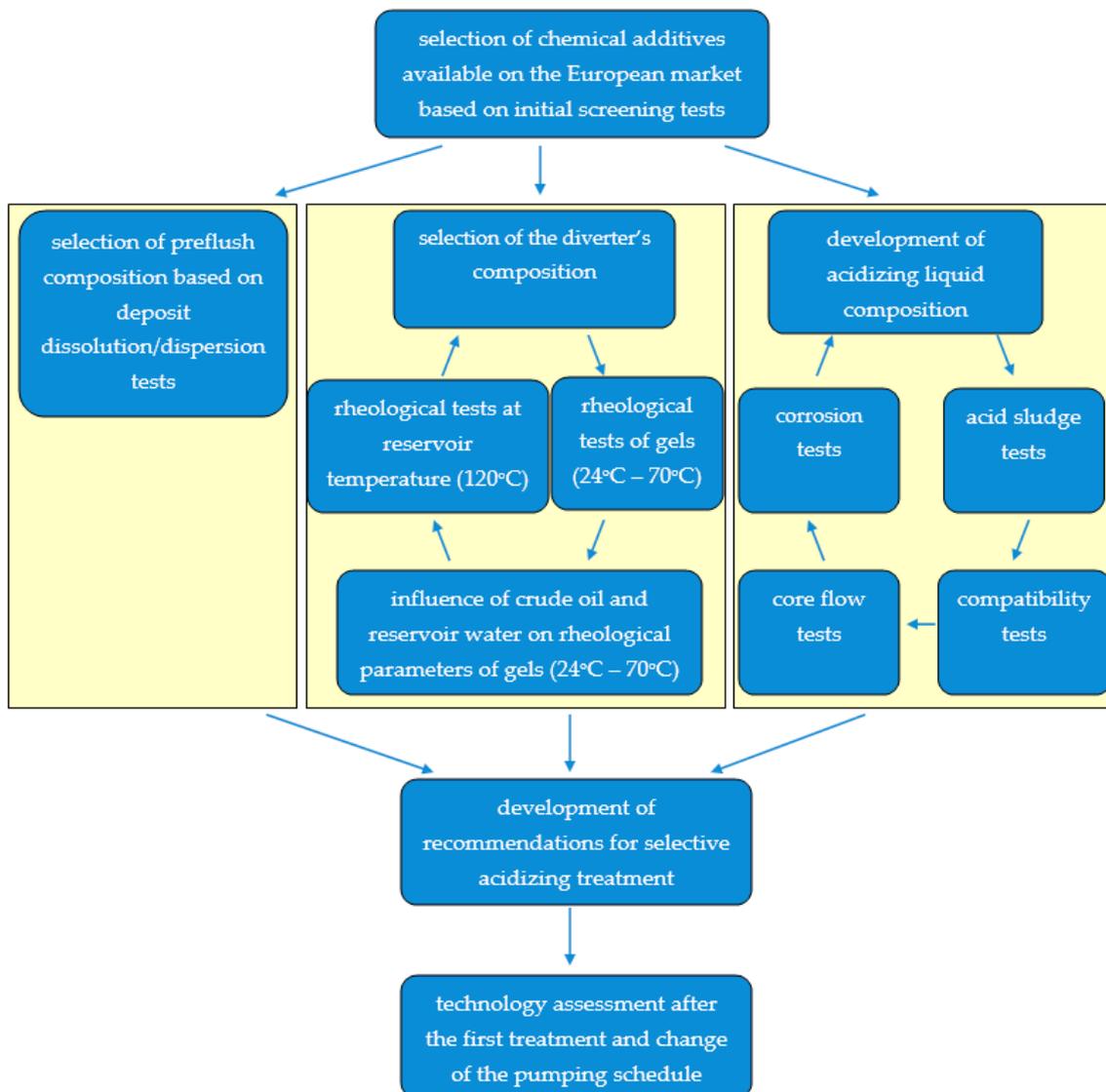


Figure 1. Flow chart diagram of the research.

2.2.1. Organic Deposit Dissolution/Dispersion Tests

The aim of these tests was to select the composition of the preflush to remove organic deposits from the pipes and the wellbore walls, which was carried out according to the following procedure. A small amount of deposit was spread on the inside wall of a 100 mL bottle, followed by the addition of 50 mL of test solution to cover about half the deposit. The contents of the bottle were gently mixed and left for 5 min, and the initial penetration of the agents was then checked. After this time, the contents of the bottle were heated to melt the deposit, and then cooled while being gently stirred. Based on this test, the following factors were assessed: penetration, dispersion, and water wetting. Penetration was determined based on de-oiling of the deposit; that is, the amount of oil floating on the test solution. The dispersion was evaluated by comparing which agents provided dispersion of the smallest particles in the liquid. After cooling of the contents of the bottle for inactive substances, re-agglomeration of the deposit occurred. An effective agent should prevent re-agglomeration by neutralizing the bonding forces of the deposit, resulting in smaller particles. In turn, water wetting was assessed based on the tendency of the deposit particles to adhere to the sides of the bottle (the less adhesion the better).

2.2.2. Rheological Tests

Rheological tests of liquids with the addition of VES were carried out using two viscometers: Fann 35SA (Fann Instrument Company, Houston, TX, USA) and HPHT NORDMAN (Nordman Instruments Inc., Houston, TX, USA). The first viscometer was used to pre-select the viscoelastic surfactant. The second was used to perform tests at the reservoir temperature (120 °C) and pressure of 2.7 MPa, which prevented boiling and evaporation of the liquid sample. Bob B5 was used in these studies, and the liquid volume was 52 cm³. These tests allowed the determination of the apparent viscosity at a shear rate of 100 s⁻¹, and additional measurements were performed every 15 min for 2 h to determine the flow consistency coefficient (k) and flow behavior index (n) according to the Ostwald-de Waele rheological model.

2.2.3. Acid Sludge Tests

The acid sludge tests were carried out according to the standard API RP 42 [35]. First, 50 cm³ of acidizing liquid was poured into a clean bottle. Then, 50 cm³ of crude oil was added, the bottle was covered and shaken vigorously. The bottle was placed in an oven at reservoir temperature (120 °C) and allowed to stand for 6 h. After this time, the mixture was poured through a clean 100-mesh stainless steel wire screen. If solids were present, the wire screen was washed with warm water to remove emulsions and paraffins. The sludge that remained on the wire screen was photographed and described.

2.2.4. Compatibility Tests

These tests were carried out to check if all components of the treatment fluids were compatible with each other. For this purpose, after preparation of liquids, it was observed whether precipitation or phase separation occurred immediately after mixing, after 2 h at ambient temperature, and after 4 h at reservoir temperature (120 °C).

2.2.5. Core Flow Experiments

Before the core flow tests, the permeability of core plugs was measured using a DGP-100 gas permeability meter (EPS, Aberdeen, UK) based on the measurement of the nitrogen flow rate and differential pressure between the inlet and outlet. The effective porosity of the core plugs was also measured using an HPG-100 helium porosimeter and a BVMS 1000 unit (both units were produced by EPS, Aberdeen, UK) to determine the total volumes of the samples. Then, the pore spaces of these core plugs were examined using X-ray microtomography (microtomograph Benchtop CT160Xi, Nikon Metrology, Tring, UK). Each core plug was placed in a core holder, connected to the flow and control system of the AFS-300 (Core Lab, Tulsa, OK, USA) unit, and sealed, as shown in Figure 2. The system was heated to the reservoir temperature (120 °C) and pumping of crude oil was initiated (interstitial velocity: 0.5 cm/min). At the same time, the back-pressure regulator was used to set the system pressure to 38 MPa. Pressure transducers were used to measure the differential pressure across the core plug. Then, one pore volume of the preflush was pumped at an interstitial velocity of 0.5 cm/min. The next stage was pumping the acidizing liquid, also at an interstitial velocity of 0.5 cm/min, until “breakthrough” was achieved; that is, the moment at which live acid exited the core plug as effluent. This usually coincided with a sudden drop in differential pressure. Then, 1 pore volume of the preflush and the crude oil were injected again. After the test, the core plug was removed from the core holder, its inlet and outlet faces were photographed, and after the core plug was dried at 115 °C, the permeability and porosity coefficients were measured again. The final stage of the test was to image the core using micro-CT to determine the structure of the wormholes.

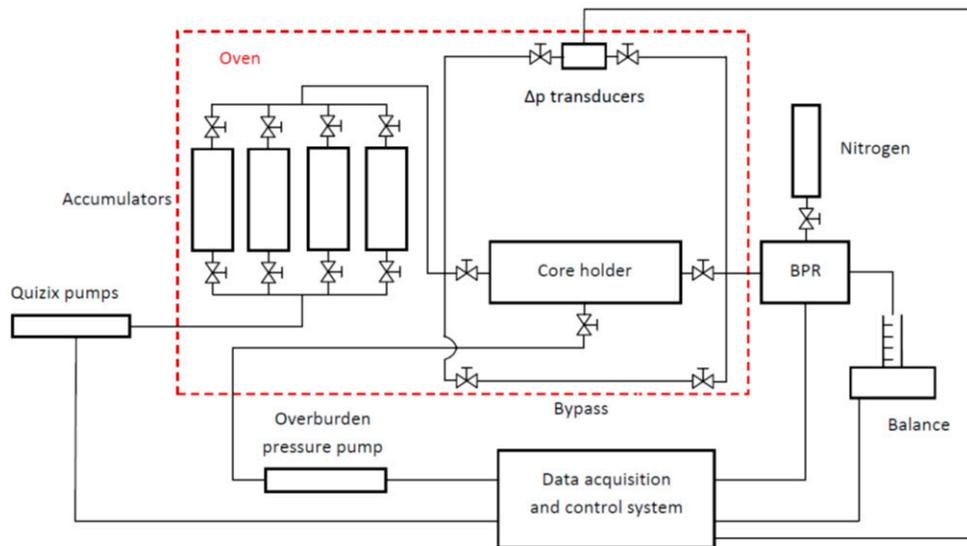


Figure 2. Coreflooding system AFS-300.

2.2.6. Corrosion Tests

Corrosion tests of the acidizing liquids were carried out in accordance with the standard ASTM G1-03 [36]. The tests were performed by immersing coupons made of L-80 steel with dimensions of 4 cm × 2 cm × 0.3 cm in the acidizing liquid under static conditions in a Hastelloy steel chamber, at a temperature of 120 °C and pressure of 40 MPa. The length of the tests was 6 h, and the ratio of the volume of acidizing liquid to the surface of the steel coupons was 7.8 cm³/cm².

3. Experimental Results

3.1. Selection of Preflush Composition

After preliminary tests, it was decided that the preflush would be prepared based on a 2% KCl solution. Then, a number of deposit dissolution/dispersion tests were conducted for various combinations and concentrations of mutual solvents (TN-16300, TN-16305, and TN-16310) and microemulsions (TN-01700 and TN-01701). The best results were obtained for a liquid containing 10% mutual solvent TN-16305 and 2% microemulsion TN-01700. The liquid did not cause de-oiling of the deposit, but after melting and re-cooling, it prevented its agglomeration into larger particles (Figure 3). To some extent, the liquid also caused the water-wetting of the surface from which the deposit was removed, which was confirmed by the adherence of only fine particles to the surface of the bottle.



Figure 3. Dissolution/sludge dispersion test results for liquids based on 2% KCl with the addition of 10% mutual solvent TN-16305 and 2% microemulsion TN-01701 (a) penetration: oil does not float on the liquid; (b) dispersion: agglomeration of small deposit particles; (c) water wetting: fine particles of the deposit adhere to the sides of the bottle.

3.2. Selection of the Diverter's Composition

Among many types of chemical agents used as diverters, the group on which particular attention was focused were viscoelastic surfactants (VES). This was due to the fact that a certain group of them is sensitive to contact with crude oil and thus potentially has the desired property. When added to an aqueous solution, their viscosity increases due to the accumulation of VES particles in larger units. Hydrocarbon chains are then associated and properly orientated to form rod-shaped structures called micelles, which form a network. Contact of such a liquid with crude oil causes breaking of large micelles down into much smaller spherical micelles, which results in a decrease in its viscosity. On the other hand, the liquid which is in contact with the reservoir water does not change its properties, as a result of which its original viscosity is maintained in the zones from which the water flows.

Viscoelastic surfactant (TN-16234, TN-16235, and TN-16237) tests were started with attempts to form gels based on a 5% hydrochloric acid solution containing a corrosion inhibitor (Brenntacor 6120LF) at a concentration of 1.0% and a corrosion inhibitor intensifier (Brenntacor AID10) at a concentration of 0.05%. The effects of viscoelastic surfactant concentrations in the ranges recommended by their producers and of crude oil and reservoir water on the viscosity of liquids were studied. The most promising results were obtained for the product TN-16235, which caused the formation of a gel. Most importantly, the viscosity of this gel decreased with the addition of crude oil, and changed only slightly after the addition of the reservoir water, as shown in Figure 4.

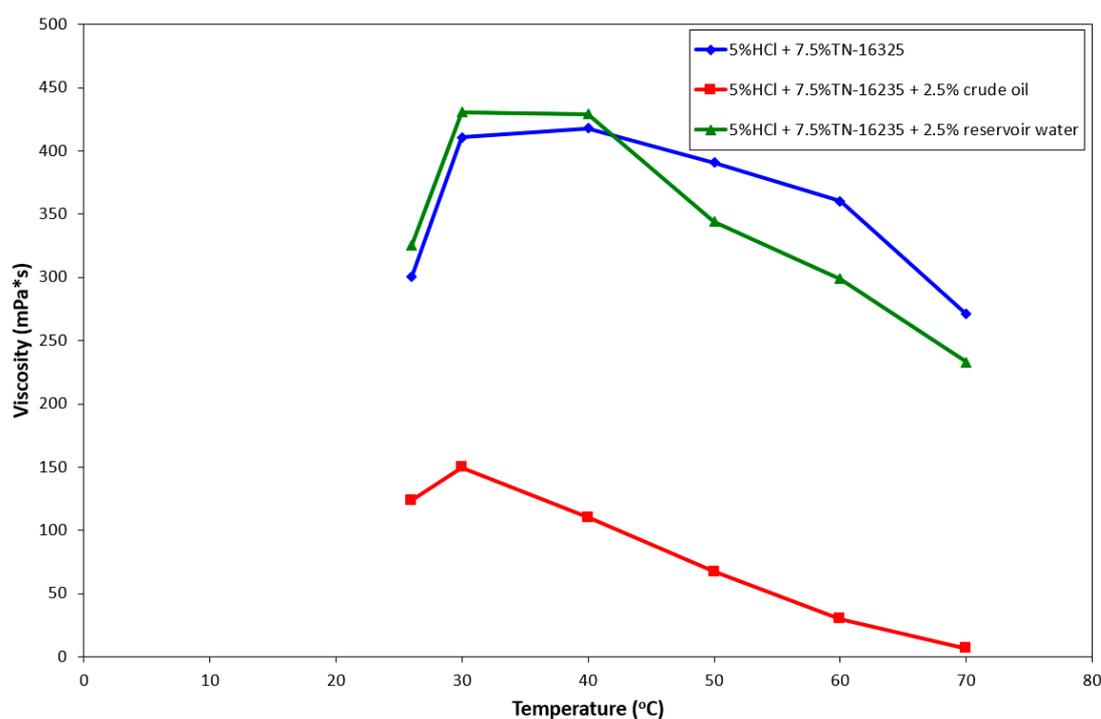


Figure 4. The effects of crude oil and reservoir water on the apparent viscosity of 5% HCl with the addition of 7.5% viscoelastic surfactant TN-16235 in a temperature range up to 70 °C at a shear rate 100 s⁻¹.

After the VES selection, further research was conducted to develop the overall composition of the liquid. Tests showed that 5% HCl solution did not provide adequate viscosity at the reservoir temperature (120 °C), despite the fact that the highest concentration (7.5%) of the VES recommended by its manufacturer was used. It was assumed that the diverter must have a viscosity above 100 mPa*s at the reservoir temperature, and that its rheological characteristics should be affected by the addition of crude oil in a small amount (2.5%). However, reservoir water should not cause a significant change in the diverter's viscosity. Therefore, after another series of tests, it was decided that a 30% solution of

calcium chloride would be used as a diverter with the addition of the viscoelastic surfactant TN-16235 at 4.5%. Figure 5 shows the rheological characteristics of this gel at the reservoir temperature of 120 °C.

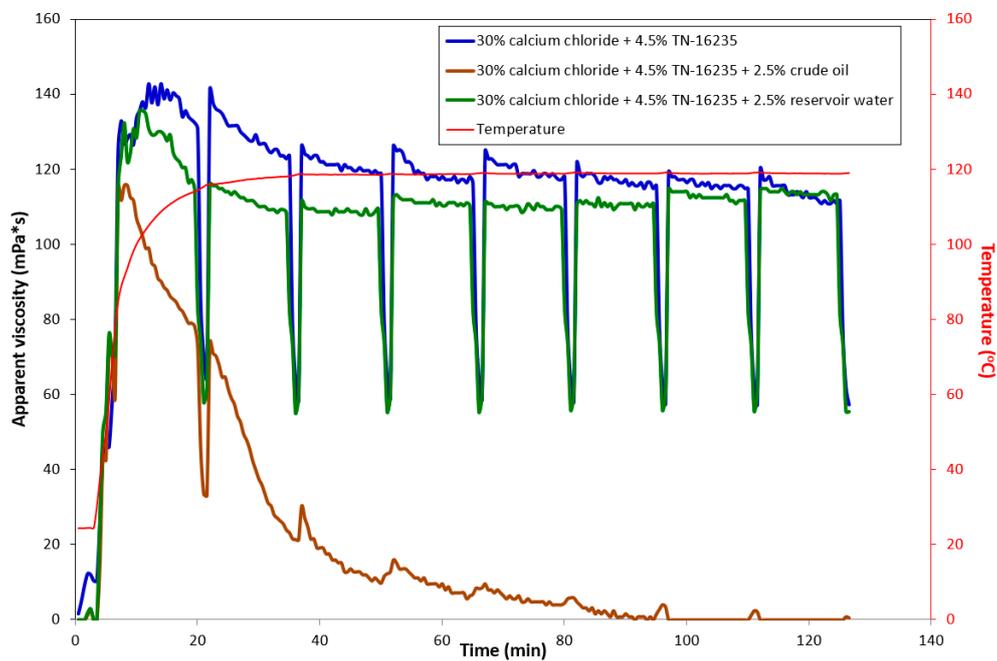


Figure 5. The effects of crude oil and reservoir water on the apparent viscosity of 30% CaCl₂ solution with the addition of 4.5% viscoelastic surfactant TN-16235 at 120 °C and at a shear rate of 100 s⁻¹.

Figure 6, in turn, shows the dependence of shear stress on shear rate for 30% CaCl₂ solution with the addition of 4.5% viscoelastic surfactant TN-16235, and Table 4 shows the values of the flow consistency coefficient (k) and flow behavior index (n).

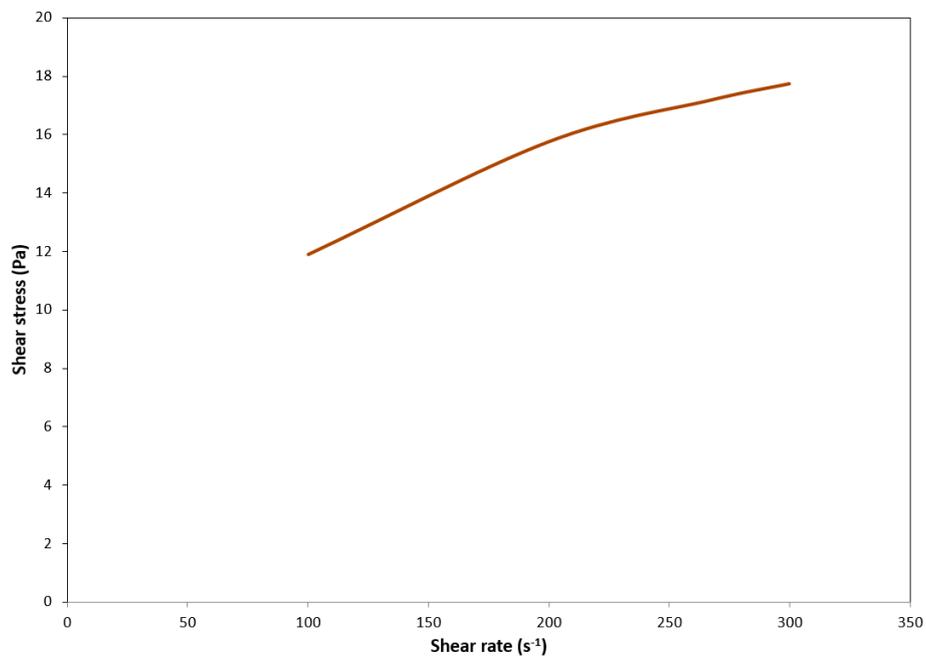


Figure 6. The dependence of shear stress on shear rate for 30% CaCl₂ solution with the addition of 4.5% viscoelastic surfactant TN-16235 at 120 °C.

Table 4. Rheological data of 30% CaCl₂ solution with the addition of 4.5% viscoelastic surfactant TN-16235 at 120 °C.

Time (min)	Temperature (°C)	30% CaCl ₂ Solution + 4.5% TN-16235		30% CaCl ₂ Solution + 4.5% TN-16235 + 2.5% Reservoir Water		30% CaCl ₂ Solution + 4.5% TN-16235 + 2.5% Crude Oil	
		n (-)	k (lbf·s ⁿ /ft ²)	n (-)	k (lbf·s ⁿ /ft ²)	n (-)	k (lbf·s ⁿ /ft ²)
2.5	24	-	-	-	-	-	-
6.5	79	1.4134	0.0001	1.3612	0.0002	1.3723	0.0002
21.5	116	0.3320	0.0600	0.3557	0.0467	0.2343	0.0546
36.5	119	0.3251	0.0581	0.3868	0.0384	0.9085	0.0007
51.5	120	0.3618	0.0476	0.3873	0.0385	1.2122	0.0001
66.5	120	0.3800	0.0428	0.3683	0.0429	1.2986	0.00003
81.5	120	0.3688	0.0451	0.3818	0.0399	1.4686	0.00001
96.5	120	0.3708	0.0442	0.3687	0.0428	-	-
111.5	120	0.3690	0.0444	0.3697	0.0426	-	-
126.5	120	0.3983	0.0377	0.3589	0.0453	-	-

Gel viscosity values were very low at ambient temperature (24 °C), therefore the HPHT NORDMAN viscometer had a problem with determining n and k because it is configured to measure more viscous liquids. Table 4 and Figure 6 show that the gel initially has a poor properties of shear thickening fluid ($n > 1$). However, at higher temperatures, above 80 °C, it changes its properties towards a shear thinning fluid ($n < 1$). The k -values for the 30% CaCl₂ solution with the addition of 4.5% viscoelastic surfactant decrease slightly with increase in temperature (from 116 °C) and test time, while n remains within the range of 0.3320 to 0.3983. The viscosity of the gel only slightly decreases at 120 °C and the liquid exhibits non-Newtonian viscous properties. Gel with the addition of 2.5% of reservoir water has similar properties. On the other hand, a 2.5% addition of crude oil causes a rapid decrease in the viscosity (at 119 °C). The liquid then exhibits Newtonian behavior (increase of n to values close to 1). The values of n higher than 1 result from the fact that the HPHT viscometer had a problem with determining n and k for low viscosity liquid.

The results of the rheological tests presented in Figure 4 indicate that a very intense increase in diverter viscosity began above 40 °C. The liquid reached its maximum viscosity at a temperature of about 100 °C, followed by a decrease in the viscosity, but it remained above 100 mPa·s at 120 °C. Even a small addition of crude oil (at 2.5%) caused a significant decrease in viscosity to values from several mPa·s to 0. However, the same amount of reservoir water caused only a slight change in viscosity compared with the reference values, which was caused by the dilution effect of the sample. Thus, the diverter showed different rheological properties depending on whether it was in contact with crude oil or reservoir water.

Most of the selective acid treatments were performed using coiled tubing and such rheological properties resulted in low flow resistance, especially on the surface. In turn, the contrast of the viscosity of the diverter in contact with reservoir water and crude oil results in that fluid may selectively block water-saturated zones while the oil-saturated zone is unaffected. As a result, the injected acidizing liquid will be directed to the oil saturated zones, where the flow resistance due to the low viscosity of the diverter will be much lower, and where stimulation is most desirable.

3.3. Development of Acidizing Liquid Composition

Development of the acidizing liquid composition was initiated by checking whether a 15% hydrochloric acid solution, based on which it was decided the liquid would be prepared, would cause precipitation of sludge from crude oil. Often, contact of crude oil with acid solutions is the cause of the precipitation of sludge, that is, organic compounds mainly consisting of asphaltenes, which significantly reduce the effectiveness of stimulation treatments. The tests showed that at reservoir temperature

(120 °C), a mixture of 15% HCl solution (containing 1% corrosion inhibitor Brenntacor 6120LF and 0.15% inhibitor intensifier Brenntacor AID10) and crude oil precipitated a moderate amount of sludge, as shown in Figure 7. After many acid sludge tests were performed, it was found that 5.5% addition of the TN-16650 agent effectively reduced sludge precipitation, as shown in Figure 8. Based on additional tests, the iron control agent TN-06740 at a concentration of 0.7% was also included in the acidizing liquid.



Figure 7. Sludge precipitated from a mixture of crude oil and 15% HCl solution.



Figure 8. Wire screen after a mixture of crude oil and 15% HCl containing 5.5% TN-16650 (anti-sludge agent) and 0.7% TN-06740 (iron control agent) was poured.

It was also decided that the viscoelastic surfactant TN-16235 would be included in the acidizing liquid at the maximum concentration of 7.5% recommended by the manufacturer. The purpose of the surfactant was to cause delay of the acid–rock reaction at the high reservoir temperature (120 °C). Reaction rate retardation took place primarily through the adsorption of this surfactant on the rock surface and creation of a barrier between the hydrochloric acid and the formation rock.

The next step in the development of the acidizing liquid composition involved testing the compatibility of all components, because the viscoelastic surfactant TN-16235 is anionic, which can cause problems in acidizing liquids (corrosion inhibitor is cationic). Tests showed that all components were compatible with each other, and no deposits were precipitated from the liquid, as shown in Figures 9 and 10.



Figure 9. Acidizing liquid with a composition of 15% HCl + 1% Brenntacor 6120LF + 0.15% Brenntacor AID10 + 5.5% TN-16650 + 0.7% TN-06740 + 7.5% TN-16235 after 2 h at ambient temperature.



Figure 10. Acidizing liquid with a composition of 15% HCl + 1% Brenntacor 6120LF + 0.15% Brenntacor AID10 + 5.5% TN-16650 + 0.7% TN-06740 + 7.5% TN-16235 after 4 h at 120 °C.

3.4. Results of Core Flow Experiments

The next stage in the research process involved performing core flow tests on dolomite core plugs. The tested core plugs were selected such that one had a lower initial permeability of 3.0 mD, whereas the second had an over tenfold higher permeability of 39.2 mD. Figures 11 and 12 show the differential pressure as a function of the injected pore volumes of fluids during the acidization of the core plugs.

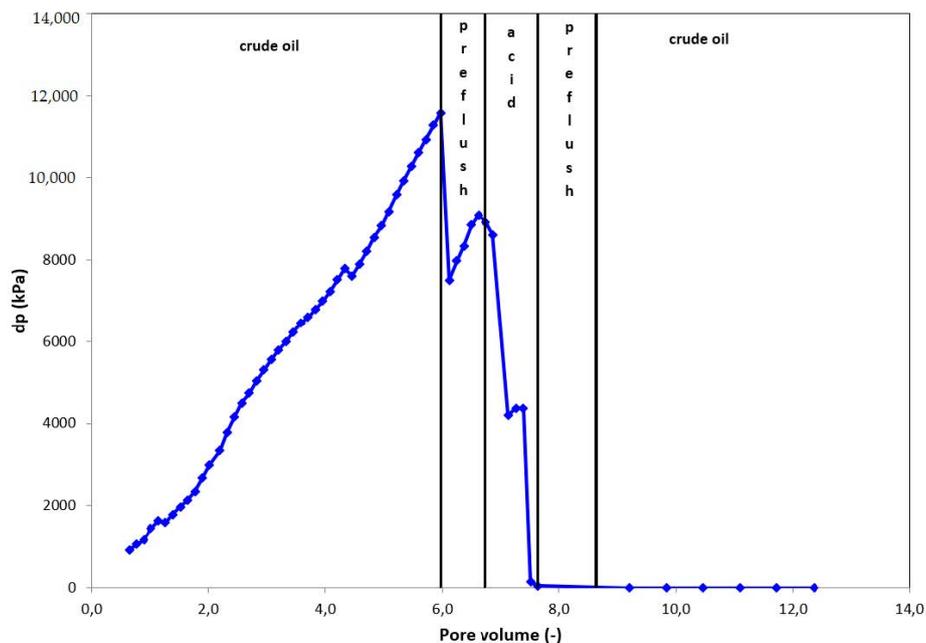


Figure 11. Differential pressure recording during the acidization of the core plug with an initial permeability of 3.0 mD. Pore volume to breakthrough (PVBT) = 0.65.

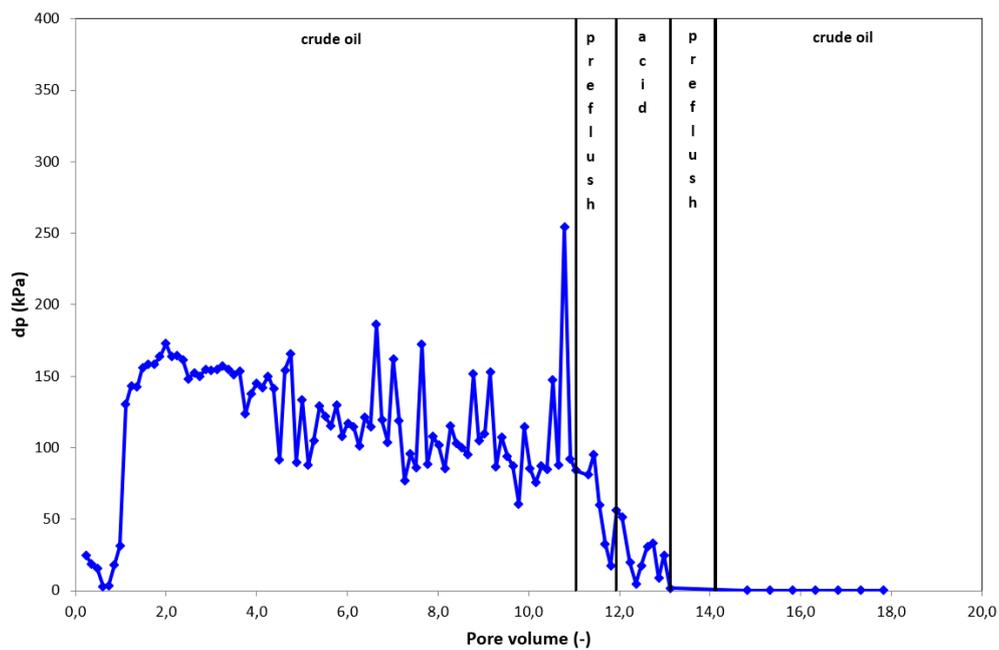


Figure 12. Differential pressure recording during the acidization of the core plug with an initial permeability of 39.2 mD. Pore volume to breakthrough (PVBT) = 0.72.

Figures 13 and 14 show photographs of the inlet and outlet faces of the core plugs after acidization.



Figure 13. Photographs of the core inlet (a) and outlet (b) faces. Core plug with an initial permeability of 3.0 mD.



Figure 14. Photographs of the core inlet (a) and outlet (b) faces. Core plug with an initial permeability of 39.2 mD.

Figures 15 and 16 show images of the pore spaces of the core plugs before and after acidization.

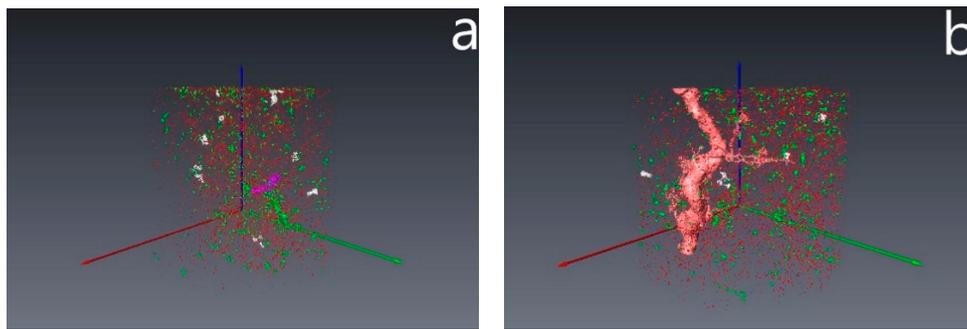


Figure 15. Images of the pore space of the core with an initial permeability 3.0 mD before (a) and after (b) acidization.

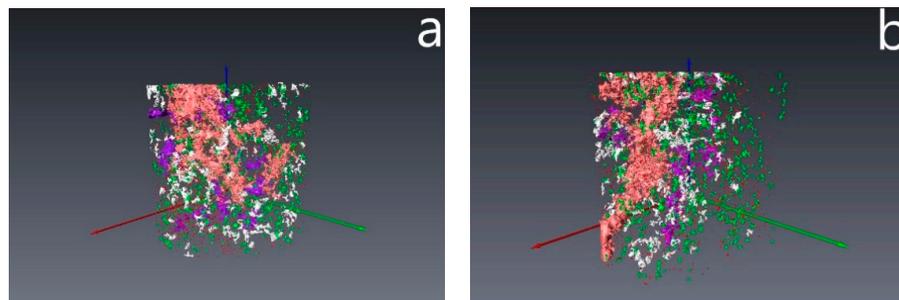


Figure 16. Images of the pore space of the core with an initial permeability 39.2 mD before (a) and after (b) acidization.

The pores presented in Figures 15 and 16 were divided into seven volume classes according to their volume (Table 5).

Table 5. Pores classification.

Volume Class (-)	Volume (Voxel)	Volume (μm^3)	Color (-)
I	1–9	2.7×10^4 – 2.7×10^5	Yellow
II	10–99	2.7×10^5 – 2.7×10^6	Cyan
III	100–999	2.7×10^6 – 2.7×10^7	Red
IV	1000–9999	2.7×10^7 – 2.7×10^8	Green
V	10,000–99,999	2.7×10^8 – 2.7×10^9	Purple
VI	100,000–400,000	2.7×10^9 – 1.08×10^{10}	Pink
VII	>400,000	$>1.08 \times 10^{10}$	Orange

The results of permeability measurements of the core plugs before and after the acidization process are presented in Table 6.

Table 6. Results of gas permeability measurements of the core plugs before and after acidization, and the pore volumes necessary for acid breakthrough (PVBT).

Nitrogen Permeability before Acidization (mD)	Nitrogen Permeability after Acidization (mD)	Stimulation Index (Permeability after/Permeability before Acidizing) (-)	PVBT (-)
3.0	190.7	63.6	0.65
39.2	604.0	15.4	0.72

Analysis of the test results should start with special attention paid to the pore volumes necessary for acid breakthrough. These values were similar in both cases and were equal to 0.65 PV for the core plug with low initial permeability (3.0 mD) and 0.72 for the core plug with higher permeability (39.2 mD). These are small values, which are beneficial because during acidizing treatment, less acid is consumed in the zone near the wellbore, and more acid is transported deeper into the formation. The same conclusion can be reached by analyzing photographs of the core faces (Figures 13 and 14), which show no signs of face dissolution; this finding indicates that the effectiveness of matrix acidizing treatment is favorable. Valuable information is also provided by the stimulation index value (SI), which for the core plug with an initial permeability of 3.0 mD was 63.6, whereas for a core with an initial permeability of 39.2 mD, it was 15.4. These are not large values, which means that little acid is used to react with the walls of the wormholes, and more is available for deeper penetration. In the case of a core with lower initial permeability, a dominant wormhole with several branches was obtained; that is, one with the best chance of extending beyond the damage zone. The number of branches was higher for the core with higher permeability, but this was because of the decidedly larger number of pores with the largest dimensions in the original structure of this rock sample (Figure 16a). The expansion of these natural branches was signaled by pressure spikes during acidizing liquid injection (Figure 12). The tested acidizing liquid system therefore has the potential to form wormhole structures that are desirable from the point of view of stimulation.

Corrosion tests were also performed and showed that the corrosion rate of the L-80 steel in the environment of this acidizing liquid at the reservoir temperature was $131.8263 \text{ g/m}^2/6 \text{ h}$. Importantly, no pitting corrosion was observed on the surfaces of the coupons after testing (Figure 17). Based on the calculated corrosion rate, it can be concluded that the weight loss of steel acceptable at this temperature equal to 244.1 g/m^2 [37], will be achieved after 11.1 h. This time is sufficient to perform the matrix acidizing treatment.



Figure 17. Photographs of corrosion coupons before (a) and after (b) test.

4. Recommendations

The tests presented in the paper allowed the development of recommendations for selective acidizing treatment.

The first five acidization treatments were carried out according to the scheme in which preflush, diverter and acidizing liquid were pumped successively, and the reservoir water was used as post flush. After the analysis of all the data collected from these treatments, it was decided to divide the total volume of diverter and acidizing liquid into smaller portions. It was also found that the viscoelastic surfactant can adsorb on the surface of the reservoir rock, which reduces the effectiveness of the treatment. Therefore, it was decided to apply a new pumping schedule. The treatment started from cleaning the wellbore of organic deposits, and for this purpose, preflush (included mutual solvent and microemulsion) circulation was used. Then, alternate pumping of the diverter and acidizing liquid was initiated. This sequence was repeated two to four times. The diverter's task was to temporarily block water-saturated zones and not block oil-saturated zones because of a significant reduction in

gel viscosity in contact with the crude oil. In turn, the acidizing liquid based on a 15% HCl solution with appropriate additives, including a surfactant, was directed to the oil-saturated zones to create wormholes. The treatment was completed by injecting the liquid, which was used as a preflush. This was done to remove the viscoelastic surfactant adsorbed on the surface of the reservoir rock. Reservoir water was used to push all the liquid out of the wellbore and into the formation. Currently, this pumping schedule is used and it brings good results.

An effective matrix acidizing treatment of carbonate reservoirs requires deep penetration of the acidizing fluid into the formation. This can be achieved by optimal propagation of the wormholes. This requires a reduction in the rate of reaction between the acid and the rock in high temperature reservoirs. Additionally, when acidizing with high water cut it is necessary to divert acidizing fluid away from water-saturated zones and into hydrocarbon-saturated zone.

5. Summary and Conclusions

The development of a fluid system for selective acidizing treatment required the solution of many research problems. The most important of them were: removal of organic deposits before treatment, thermal stability and compatibility of liquid components, sludge formation, acid corrosion, proper penetration of the acidizing liquid into the formation and above all, the appropriate rheological properties of the diverter. A mixture of mutual solvent and microemulsions has been prepared for the removal of organic deposits.

The test results presented in this paper confirmed the usefulness of the viscoelastic surfactant TN-16235 sensitive to crude oil for performing selective acidizing of the oil field in the Zechstein Main Dolomite. Surfactant was added to two liquids: to the diverter as the main additive at a concentration of 4.5%, and to the acidizing liquid at a concentration of 7.5%. The first of these liquids forms a viscous gel at the reservoir temperature and temporarily plugs water-saturated zones diverts acidizing liquid into damaged oil-saturated zones. The development of the liquid composition required a series of compatibility tests because the viscoelastic surfactant is anionic. The selected corrosion inhibitor—intensifier system allowed for a sufficiently long corrosion protection to perform acidizing treatment. An anti-sludge additive and iron control agent were also selected. The developed system ensures proper penetration of the acidizing liquid into the formation. The core flow tests showed that dominant wormholes are formed at the reservoir temperature (120 °C). This channel structure represents the best dissolution model for a given rock-acidizing liquid under given reservoir conditions. This was achieved by using a viscoelastic surfactant TN-16235 that acts as a chemical retarder. TN-16235 coats the pore surfaces and creates a barrier between the live acid and the formation rock. This allows the live acid to penetrate deeper. In order to remove this film, it is necessary to use a mixture of mutual solvent and microemulsion at the end of the treatment.

Since 2015, 28 acidizing treatments have been performed according to this technology. Most of these treatments confirmed the effectiveness of the developed technology. The near-wellbore damage was removed without increasing water cut, which has been a fundamental problem for this oil field to date. It should be emphasized that the composition of the fluid system used in the selective acidizing technology and pumping schedule can be modified to the given reservoir conditions.

Author Contributions: Conceptualization, investigation, supervision, results interpretation, manuscript writing, M.C.; investigation, interpretation, editing, P.K.; supervision, project administration, funding acquisition, Ł.L. All authors have read and agreed to the published version of the manuscript.

Funding: The research was cofounded by Brenntag Polska.

Acknowledgments: We want to thank for Oil and Gas Institute–National Research Institute management for supporting us during this project, and Brenntag Polska for funding acquisition, administration of the project, and support of this research.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

PV	Pore Volume
PVBT	Pore Volume to Breakthrough
SI	Stimulation Index

References

1. Allen, T.O.; Roberts, A.P. *Production Operations*; Oil & Gas Consultants International: Tulsa, OK, USA, 1993; Volume 2.
2. Ott, W.K. *Well Stimulation: Acidizing and Hydraulic Fracturing*; IHRDC: Boston, MA, USA, 1991.
3. Nasr-El-Din, H.A.; Al-Mohammad, A.M.; Al-Aamri, A.D.; Al-Fuwaires, O. Reaction of Gelled Acids with Calcite. *SPE Prod. Oper.* **2008**, *353–361*. [[CrossRef](#)]
4. Fu, D.; Chang, F. Compositions and Methods for Treating a Subterranean Formation. WIPO Patent 2004/005671, 15 January 2004.
5. Buijse, M.A.; de Boer, P.; Breukel, B.; Klos, M.; Burgos, G. Organic Acids in Carbonate Acidizing. In Proceedings of the SPE European Formation Damage Conference, Hague, The Netherlands, 13–14 May 2003. [[CrossRef](#)]
6. van Domelen, M.S.; Jennings, A.R. Alternate Acid Blends for HPHT Applications. In Proceedings of the Offshore Europe, Aberdeen, UK, 5–8 September 1995. [[CrossRef](#)]
7. Alkhalidi, M.H.; Nasr-El-Din, H.A.; Sarma, H. Kinetics of the Reaction of Citric Acid with Calcite. *SPE J.* **2010**, *15*, 704–713. [[CrossRef](#)]
8. Fredd, C.N.; Fogler, H.S. Alternative Stimulation Fluids and their Impact on Carbonate Acidizing. *SPE J.* **1998**, *3*, 34–41. [[CrossRef](#)]
9. Fredd, C.N.; Fogler, H.S. The Influence of Chelating Agents on the Kinetics of Calcite Dissolution. *J. Colloid Interface Sci.* **1998**, *204*, 187–197. [[CrossRef](#)] [[PubMed](#)]
10. Rabie, A.I.; Mahmoud, M.A.; Nasr-El-Din, H.A. Reaction of GLDA with Calcite: Reaction Kinetics and Transport Study. In Proceedings of the SPE International Symposium on Oilfield Chemistry, The Woodlands, TX, USA, 11–13 April 2011. [[CrossRef](#)]
11. Dill, W.R.; Keeney, B.R. Optimizing HCl-Formic Acid Mixtures for High Temperature Stimulation. In Proceedings of the SPE Annual Fall Technical Conference and Exhibition, Houston, TX, USA, 1–3 October 1978. [[CrossRef](#)]
12. Katheeri, M.; Nasr-El-Din, H.A.; Taylor, K.C.; Grainees, A.H. Determination and Fate of Formic Acid in High Temperature Acid Stimulation Fluids. In Proceedings of the International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, USA, 20–21 February 2002. [[CrossRef](#)]
13. Taylor, K.C.; Al-Katheeri, M.I.; Nasr-El-Din, H.A. Development and Field Application of a New Measurement Technique for Organic Acid Additives in Stimulation Fluids. *SPE J.* **2005**, *10*, 152–160. [[CrossRef](#)]
14. Buijse, M.A.; van Domelen, M.S. Novel Application of Emulsified Acids to Matrix Stimulation of Heterogeneous Formations. In Proceedings of the SPE Formation Damage Control Conference, Lafayette, LA, USA, 18–19 February 1998. [[CrossRef](#)]
15. Rabie, A.I.; Gomaa, A.M.; Nasr-El-Din, H.A. Determination of Reaction Rate of In-Situ Gelled Acids with Calcite Using the Rotating Disk Apparatus. In Proceedings of the SPE Production and Operations Conference and Exhibition, Tunis, Tunisia, 8–10 June 2010. [[CrossRef](#)]
16. Nasr-El-Din, H.A.; Al-Mohammad, A.M.; Al-Aamri, A.D.; Al-Fahad, M.A. Quantitative Analysis of Reaction-Rate Retardation in Surfactant-Based Acids. *SPE Prod. Oper.* **2009**, *24*, 107–116. [[CrossRef](#)]
17. Crowe, C.W.; Miller, B.D. New, Low-Viscosity Acid-In-Oil Emulsions Provide High Degree of Retardation at High Temperature. In Proceedings of the SPE Rocky Mountain Regional Meeting, Billings, MT, USA, 15–16 May 1974. [[CrossRef](#)]
18. Sayed, M.A.; Nasr-El-Din, H.A. Reaction Rate of Emulsified Acids and Dolomite. In Proceedings of the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, USA, 15–17 February 2012. [[CrossRef](#)]
19. Sayed, M.A.; Nasr-El-Din, H.A.; Nasrabadi, H. Reaction of Emulsified Acids with Dolomite. *J. Can. Pet. Technol.* **2013**, *52*, 164–175. [[CrossRef](#)]

20. Chang, F.F.; Nasr-El-Din, H.A.; Lindvig, T.; Qiu, X.W. Matrix Acidizing of Carbonate Reservoirs Using Organic Acids and Mixture of HCl and Organic Acid. In Proceedings of the SPE Annual Technical Conference and Exhibition, Denver, CO, USA, 21–24 September 2008. [[CrossRef](#)]
21. Ortega, A.; Nasr-El-Din, H.A.; Rimassa, S. Acidizing High Temperature Carbonate Reservoirs Using Methanesulfonic Acid: A Coreflood Study. In Proceedings of the American Association of Drilling Engineers Fluids Technical Conference and Exhibition, Houston, TX, USA, 15–16 April 2014.
22. Rabie, A.I. Reaction of Calcite and Dolomite with In-Situ Gelled Acids, Organic Acids, and Environmentally Friendly Chelating Agent (GLDA). Ph.D. Thesis, Texas A&M University, College Station, TX, USA, 2012.
23. Chen, Y.; Mahdi, A.; Marcinew, R.; Graham, M.; Pope, T.L. Viscoelastic Surfactant Acid Treatment. U.S. Patent 8,895,481, 25 November 2014.
24. Fu, D.; de Victoria, M.G.-L. Viscoelastic Acid. U.S. Patent 2005/0126786, 16 June 2005.
25. Fu, D.; Panga, M.; Kefi, S.; de Victoria, M.G.-L. Self Diverting Matrix Acid. U.S. Patent 2006/0081370, 20 April 2006.
26. Pandya, N.K.; Wadekar, S.D.; Pathre, G.S. Branched Viscoelastic Surfactant for High-Temperature Acidizing. U.S. Patent 2014/0246198, 4 September 2014.
27. Plasier, R.C.; Allen, S.R. Surfactant Based Viscoelastic Fluids and Methods of Using the Same. U.S. Patent 8,196,662, 12 June 2012.
28. Qu, Q.; Alleman, D. Acid Diverting System Containing Quaternary Amine. U.S. Patent 7,115,546, 3 October 2006.
29. Wadekar, S.D.; Pandya, N.K.; Salgaonkar, L.P.; Sabhapondit, A. Cationic Viscoelastic Surfactant with Non-Cationic Corrosion Inhibitor and Organic Anion for Acidizing. U.S. Patent 2014/0256604, 11 September 2014.
30. Welton, T.D.; Lewis, S.J.; Funkhouser, G.P. Viscoelastic Surfactant Fluids and Associated Acidizing Methods. U.S. Patent 7,159,659, 9 January 2007.
31. Kelland, M.A. *Production Chemicals for the Oil and Gas Industry*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2014.
32. Chang, F.F.; Love, T.; Affeld, C.J.; Blevins, J.B., III; Thomas, R.L.; Fu, D.K. Case Study of a Novel Acid-Diversion Technique in Carbonate Reservoirs. In Proceedings of the SPE Annual Technical Conference and Exhibition, Houston, TX, USA, 3–6 October 1999. [[CrossRef](#)]
33. Holt, S.; Zhou, J.; Gadberry, F.; Nasr-El-Din, H.; Wang, G. A Novel Viscoelastic Surfactant Suitable for Use in High Temperature Carbonate Reservoirs for Diverted Acidizing Stimulation Treatments. In Proceedings of the Rio Oil & Gas Expo and Conference 2012, Rio de Janeiro, Brazil, 17–20 September 2012.
34. Kasza, P.; Dziadkiewicz, M.; Czupski, M. From Laboratory Research to Successful Practice: A Case Study of Carbonate Formation Emulsified Acid Treatments. In Proceedings of the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, USA, 15–17 February 2006. [[CrossRef](#)]
35. API, R.P. Recommended Practices for Laboratory Evaluation of Surface Active Agents for Well Stimulation. In *API RP 42*, 2nd ed.; American Petroleum Institute (API): Washington, DC, USA, 1977.
36. ASTM G1-03(2017)e1. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*; ASTM International: West Conshohocken, PA, USA, 2017. [[CrossRef](#)]
37. Smith, C.F.; Dollarhide, F.E.; Byth, N.J. Acid Corrosion Inhibitors—Are We Getting What We Need? *J. Pet. Technol.* **1978**, *30*, 737–746. [[CrossRef](#)]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).