UDC 622.06
DOI: 10.15587/1729-4061.2024.305373

INCREASING THE EFFICIENCY OF STIMULATION OF COMPACTED CARBONATE RESERVOIRS WITH ACID SOLUTIONS BASED ON METHYL ACETATE

Ivan Zezekalo
Doctor of Technical Sciences, Professor*
Oleh Zimin
Corresponding author
PhD Student*
E-mail: oleg.zimin.geo@gmail.com
Yuliya Laziebna
PhD Student*
*Department of Oil and Gas Engineering and Technology
National University "Yuri Kondratyuk Poltava Polytechnic"
Pershotravnevyi ave., 24, Poltava, Ukraine, 36011

The development of oil and gas deposits in compacted rocks is a promising area of development in the oil and gas industry. The object of research in this paper is the filtration properties of compacted rocks. To develop such deposits, special extraction technologies are required. Compacted carbonate rocks are easily dissolved by most acids, but for effective use, it is necessary that working solutions have very low viscosity and surface tension coefficient. Special filtration equipment has been developed for the research, which allows pumping various liquids and gases through rock samples and measuring permeability at pressures up to 1,000 bar.

To determine the effectiveness of the acid solution, three groups of samples were studied: silty sandstone with clay-carbonate cement with a permeability of 0.2–0.95 mD, compacted organogenic-detrital light gray limestone with a permeability of 0.001–0.004 mD, and organogenic-detrital gray limestone with a permeability of 0.04–0.06 mD. In the course of the study, the stimulation fluid was pumped through the samples at a pressure of 200–300 bar and a temperature of 120 °C. The efficiency was determined by the change in nitrogen permeability of the samples before and after the experiments. In general, the studied stimulation fluid allowed increasing the permeability of rocks up to 3–7 times, depending on the rock and research conditions. The solution retains its reactivity for a long time and, due to its low viscosity and surface tension, penetrates deeply into the rock and significantly increases the well treatment radius compared to conventional acid treatments. The use of the developed acid solution for well stimulation will increase the efficiency of hydrocarbon production from compacted reservoirs without the use of hydraulic fracturing

Keywords: carbonate reservoirs, compacted rocks, well stimulation, improved acid treatment of wells

Received date 21.03.2024
Accepted date 31.05.2024
Published date 28.06.2024

How to Cite: *Zezekalo, I., Zimin, O., Laziebna, Y. (2024). Increasing the efficiency of stimulation of compacted carbonate reservoirs with acid solutions based on methyl acetate. Eastern-European Journal of Enterprise Technologies, 3 (6 (129)), 36–43. https://doi.org/10.15587/1729-4061.2024.305373*

1. Introduction

Significant prospects for increasing recoverable oil and gas reserves are offered by the possibility of developing deep-seated compacted rocks with high reservoir pressures and temperatures and low filtration and reservoir capacity characteristics, which have difficult operating conditions. The development of unconventional hydrocarbon sources is developing rapidly in the world: shale gas and oil, gas from compacted terrigenous and carbonate reservoirs, etc. [1, 2].

According to preliminary estimates, for example, in Ukraine, recoverable gas reserves in compacted gas reservoirs may range from 1.5 to 8.5 trillion m^3 [3]. Unlike shale rocks, the study of unconventional hydrocarbon accumulations in compacted carbonate rocks is only at the development stage. Oil and gas saturated carbonate deposits in the Dnipro-Donetsk Basin are concentrated mainly in the Lower Carboniferous and Upper Devonian deposits. The deposits can be classified as highly promising, as they have a significant planar distribution and a productive thickness of up to several hundred meters. However, the properties of compacted hydrocarbon deposits are very variable and have a wide range of permeability and porosity with increasing depth [3]. With an average porosity value of 2 to 6 %, the permeability can be in the range of 0.005–0.1 mD. Often, rocks have high chemical activity, which leads to rapid contamination of the bottomhole zone during primary and secondary formation opening [4]. Consequently, further efficient operation requires stimulation to improve reservoir permeability, but high temperatures and pressures at depths of more than 5,000 meters require improvement of existing development and stimulation technologies. Therefore, research on the development of new solutions for the stimulation of hydrocarbon production is relevant.

2. Literature review and problem statement

Carbonate rocks are dissolved by most acids, but the choice of an effective stimulation technology depends on a large number of factors. The optimal approach to choosing a stimulation technology is based on taking into account the effective thickness of the productive horizon, rock composition, chemical properties of the fluid and rock, temperature, pressure, filtration and capacitive characteristics, and the causes of low formation permeability. The paper [5] analyzes the complex porous rock environment and identifies patterns that allow predicting the movement of fluids in rocks. However, studies also indicate the need for laboratory experiments when modeling filtration processes, especially for conditions of complex pore space.

An analysis of enhanced oil recovery (EOR) technologies in complex geological conditions [6] shows that most carbonate reservoirs are effectively stimulated by various technologies. However, the efficiency of such stimulation decreases with increasing depth and complication of the porous medium structure. Gas methods of enhanced oil recovery have better performance than, for example, chemical methods, but the low permeability of the bottomhole zone still requires drilling more wells. This can be prevented by improving the permeability of the bottomhole zone of the formation using deep-penetrating acid treatment.

In [7], a comparative analysis of the effectiveness of matrix acid treatment and acid fracturing was conducted. It is shown that under conditions of low permeability, acid fracturing is an effective method of stimulation, and conventional acid treatments may not be effective. The disadvantage of acid fracturing is often technological limitations of the well or bottomhole zone. Studies of the reaction kinetics of HCl solution [8] show that the reaction rate is affected by temperature, viscosity and concentration of acid, rock structure, impurities in the composition, and injection rate. It follows from the publication that the use of a hydrochloric acid-based solution is impractical for stimulating a carbonate reservoir with very low permeability and a significant content of additional impurities in the rock.

The work [9] shows that traditional treatment models involve injecting significant volumes of acid and require accurate predictions and experiments before starting the treatment process. The developed treatment model is quite accurate in predicting carbonate deposits with variable porosity, but does not answer the question of what to do with rocks of ultra-low porosity and permeability. The high rate of acid reaction with carbonate rock in compacted rocks is a negative factor, as the mixture loses its reactivity in the bottomhole zone. If the stimulation fluid erodes cavities only near perforations or filter holes, such treatment hardly changes the well's efficiency. Studies [10] show that a significant number of different inhibitors and stabilizers are used to increase the efficiency of treatments, which generally negatively affect the treatment efficiency in conditions of low permeability and high temperatures. This requires the use of solutions that would initially have low corrosion activity and a slow reaction rate at high temperatures. The work [11] shows that iron compounds such as pyrite and siderite pose a danger during acid treatment. Acid reactions with these compounds are very diverse and poorly predictable, as they depend on temperature, concentrations, the presence of additional impurities, fluid properties, and other factors. Mostly, the presence of these impurities in the rock is a negative factor that leads to a decrease in filtration characteristics after treatment, as it leads to precipitation of iron compounds as a result of primary, secondary and tertiary reactions. The results show that chelating agents minimize iron precipitation, but can combine with Ca+ and Mg+ during treatment.

Thus, the effect of matrix treatment of carbonate rocks is observed mainly within a radius of up to a meter, which is often not enough for high-quality treatment of the bottomhole zone (BHZ) and reduction of the skin effect. This suggests that for efficient well operation in compacted rocks, a significant increase in permeability within a radius of tens of meters is necessary, which requires the use of slow-reaction and low-viscosity solutions.

The study [12] investigated the use of solutions with low viscosity, low surface tension coefficient, and slow reaction rate with rock to stimulate oil and gas production from compacted low-permeability, high-temperature carbonate reservoirs. Methyl acetate was chosen as the most promising acid carrier among the liquids studied and analyzed. The stimulation solutions showed their efficiency and low reaction rate at temperatures up to 120 °C on chalk plates and artificial core samples.

Therefore, to confirm the effectiveness of acid solutions based on methyl acetate and carboxylic acids, it is necessary to study their effect on carbonate rocks in reservoir conditions.

3. The aim and objectives of the study

The aim of the study is to increase the permeability of compacted carbonate rocks and terrigenous rocks with a high carbonate content by using an acid solution based on acetic acid and methyl acetate. This will make it possible to effectively use the developed solutions for the stimulation of high-temperature, low-permeability carbonate rocks.

To achieve this aim, the following objectives were accomplished:

– to study the effect of methyl acetate on the efficiency of penetration into real rocks at high reservoir pressures and temperatures;

– to study the effect of the developed solution on low-permeability rocks with different filtration and capacitance characteristics (FCC).

4. Materials and methods of research

The object of research in this paper is filtration processes in compacted rocks. The main hypothesis of the work is the ability of acid solutions based on organic or inorganic acids to dissolve the carbonate component in rocks, which increases the permeability of these rocks. The study takes into account the assumption that reducing the viscosity and slowing down the reaction of the active acid solution leads to an increase in the radius of processing the compacted rock in the bottomhole zone. The study [12] proved the effectiveness of using solutions at temperatures from 25 to 120 °C, so the simplification of this experiment is to use solutions in the recommended concentrations [13] at sample temperatures of 120 °C.

Specialized filtration equipment has been developed to study filtration processes in rocks [14].

The low-pressure filtration unit allows for standard FCC studies, i.e. pumping various gases, liquids, and solutions through rock samples or artificial cylindrical cores of 30×30 mm in size. The unit is also used to quickly assess the impact of stimulation, killing, and other process fluids on the capacitive properties of rocks at pressures up to 10 MPa and temperatures up to 120 °C.

The advantages of the low-pressure filtration unit are the high speed of porosity and permeability measurements. The core holder is pressurized with air and can be quickly disassembled for sample replacement. The equipment does not require complicated preparatory work and cleaning before each operation, unlike equipment that runs on technical oil.

This allows for dozens of tests per day to perform a variety of evaluation tests.

For filtration studies at high reservoir pressures and temperatures, a more sophisticated and technologically advanced HPHT filtration system was developed. The equipment is designed primarily for accurate determination of the FCC over a wide range of pressures and temperatures, and for studying the impact of various mining technologies and production stimulation methods on rock samples (Fig. 1).

The main element of the system is a core holder, into which samples are loaded. They are placed in the cuff, which allows creating a compression pressure of 110 MPa. The system has two pumps for pumping various process fluids through the samples. The high-pressure pump is designed to create operating pressures of up to 100 MPa. The M480 HPLC pump has high flow accuracy and operates at pressures up to 40 MPa. To create the reservoir temperature, a heat-insulating casing with heating elements is used to heat the core holder and fluid supply lines to 200 °C.

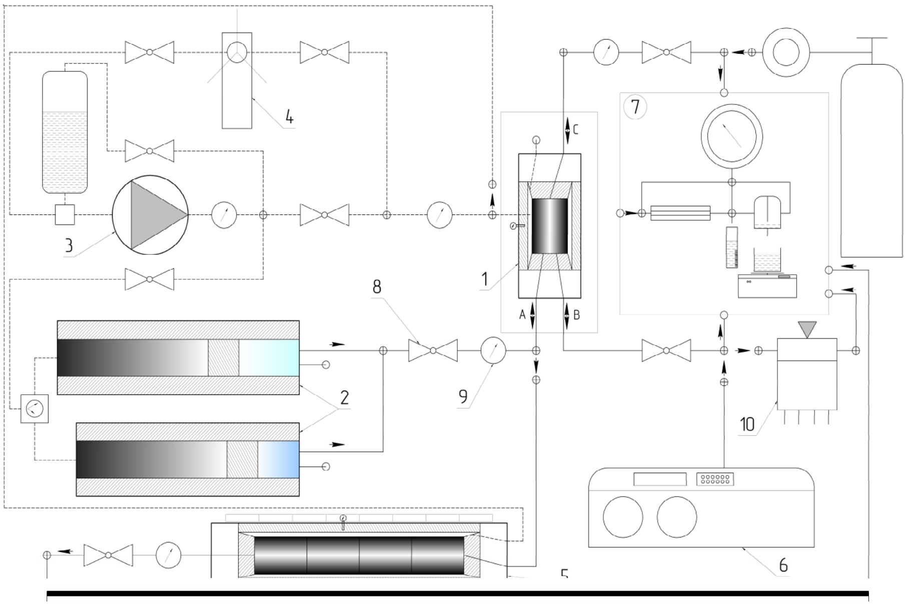


Fig. 1. Scheme of high-pressure filtration system: 1 – core holder; 2 – press separators; 3 – high-pressure oil pump; 4 – manual press; 5 – horizontal set core holder; 6 – high-pressure precision pump; 7 – measuring unit; 8 – valves; 9 – pressure sensors; 10 – backpressure regulator

Experiments to determine the filtration and capacitance characteristics of the core material, as well as the process of core treatment with a stimulation fluid, are carried out in a stationary filtration mode. Depending on the filtration mode, the process of fluid filtration through a porous medium can be described by the linear Darcy's law of filtration or by a nonlinear law. Fluid filtration is carried out in the axial direction.

On the basis of previous research and development [12, 13], we tested the developed stimulation fluid with the working name SF-1 of the following composition: acetic acid – 20 %, surfactant Solpen-10 – 0.5 %, methyl acetate – the rest.

The developed acid solution was preliminarily tested on samples of artificial carbonate core at filtration units. The research involved pumping solutions at temperatures up to 120 °C through sandstone samples to determine the dependence of filtration performance on temperature.

To confirm the effectiveness of the developed acid solutions, further studies based on methyl acetate and carboxylic acids were conducted on cores of compacted rocks in reservoir conditions. Three groups of samples of the most typical composition and properties for compacted carbonate reservoirs were used for the study:

1. Sample group No. 1 (sample numbers 2,131–2,139) is a fine-grained, silty polymictic sandstone with clay-carbonate cement, the depth of sampling is 4,850-4,878 m (Fig. 2).

The structure is psamite, the texture is disordered. The composition of the rock is quartz 80 %, mica 5 %, cement 15 %. Quartz 0.03–0.15 mm in size (0.03–0.05 fraction accounts for about 10 %), irregular, isometric and elongated grains, semicircular, angular, medium-sorted, with gas-liquid inclusions, some of them have regeneration rims.

The cement is open-pore, basal in some areas, carbonate represented by calcite-ankerite, lesser amounts of siderite, accounting for 15 %, clay kaolinite and lesser amounts of pyrite, accounting for 5 %. The pores of the kaolinite are clean and transparent. Carbonation is 4.2 %, open porosity is 6.2 %, and permeability is 0.95 mD.

2. Sample group No. 2 (1,132–1,145) is a light gray organogenic detrital limestone, sampling depth 5,024–5,090 m (Fig. 3).

The structure is organogenic detrital, the texture is disordered. The rock is composed of 50 % paleontological remains, 50 % is composed of fine-crystalline calcite. Crystals are irregular and diamond-shaped. The fauna is represented by foraminifera shells, fragments of algae, corals, crinoids, brachiopod shells, shell detritus replaced by isomorphic and medium-crystalline calcite. There is a branched calcite-mineralized fracture, with openings of 0.5 mm, 0.3 mm, 0.2 mm.

Carbonate content – 51 %, open porosity – 2.5–2.8 %, permeability – 0.001–0.004 mD.

3. Sample group No. 3 (1,180–1,188) is gray organogenic detrital limestone, sampling depth 4,650–4,750 m (Fig. 4).

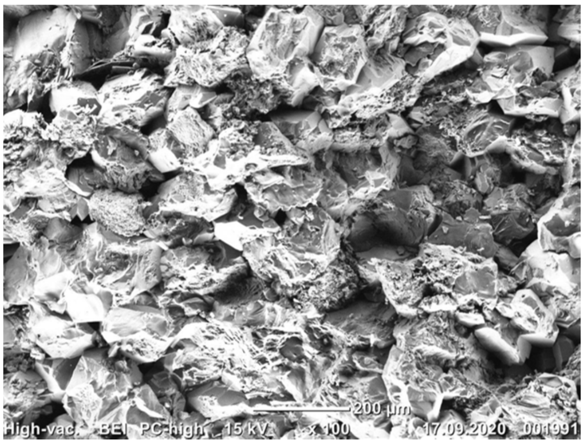
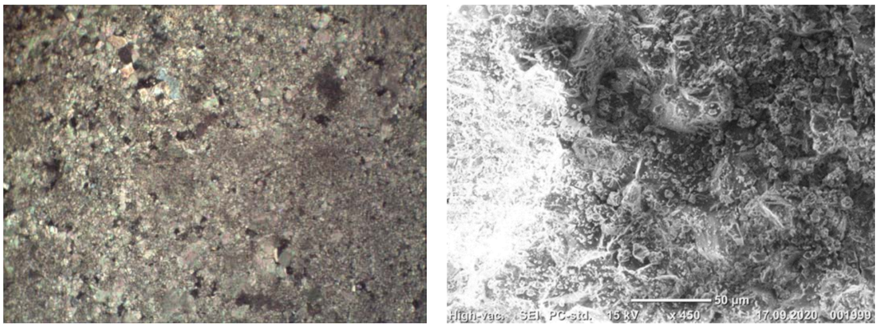


Fig. 2. Sample group No. 1 (results of the study on the JCM-6000 electron microscope)



a *b*

Fig. 3. Sample group No. 2 Light gray organogenic detrital limestone: *a* — grinding image; *b* — electron microscope image

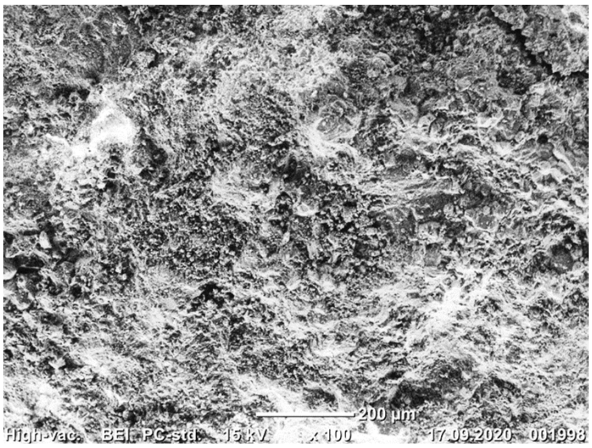


Fig. 4. Sample group No. 3 Gray organogenic detrital limestone

The structure is organogenic-detrital, the texture is disordered. The rock is composed of 40 % paleontological remains, up to 50 % fine- and medium-crystalline calcite, and up to 15 % dolomite. The crystals are irregular in shape. The fauna is represented by brachiopod shells, shell detritus replaced by isomorphic and medium-crystalline calcite. There are branched fractures partially mineralized with calcite, up to 0.3 mm open. Carbonate content is 68 %, open porosity is 5.6 %, permeability is 0.04–0.06 mD.

The tests are performed as follows. A standard cylindrical core sample of 30*30 mm is loaded into the core holder (1), which is connected to the feed line (A) and the measuring unit (7) through the line (C). The core holder is lubricated to create lateral (rock) pressure using a press (4). The stimulation fluid is poured into the working part of the separator (2) and the pump (3) is used to supply the technical part of the separator (2) with lubricant. The solution begins to be forced out of the separator through the working pipelines through the sample in the core holder. At the same time, the pressure parameters at the inlet and outlet of the core holder are monitored by sensors (9). The temperature is measured and set by the controller and maintained by a heater in the casing. In the measuring unit, the heated waste fluid leaving the core holder passes through the refrigerator and enters the measuring container, which, if necessary, is placed on a scale to record the flow rate over time. After the injection process is completed, the line (C) is connected to the nitrogen supply line from a high-pressure cylinder. The gas from the cylinder is pumped at a given pressure through the core in the opposite direction to remove residual solution and reaction products by the gas phase. The measuring unit (7) is connected to the core holder line (B), the gas-liquid mixture passes through the separator, and after liquid separation, the gas volume is measured by a mass gas flow meter.

All data is promptly measured, stored and analyzed using a SCADA system, on the basis of which analytical graphs of the effect of the developed solution on rock samples are built.

When studying the effectiveness of methyl acetate on the filtration properties of an acid solution, a study of classical stimulation fluids was initially conducted: 8 % aqueous solution of inhibited hydrochloric acid and 15 % aqueous solution of acetic acid. The study was carried out at a pressure of 19–20 MPa at a temperature of 120 °C on carbonate rocks with a permeability of 0.01–0.05 mD from the sample group No. 2 and No. 3.

To investigate the effectiveness of the investigated SF-1 solution, pumping was performed on sample group No. 1 with a permeability of 0.2 to 1 mD at a pressure of 19–21 MPa on average and a temperature of 120 °C. A total of 9 tests were conducted with similar parameters.

Sample group No. 2 is represented by ultra-low permeability limestone, represented by samples 1,132–1,136 from the upper part of the core, which are characterized by a calcite-mineralized microfracture, which, by the way, does not affect the initial permeability. As well as samples from the lower part of the core 1,137-1,145, which have no fractures (except for sample 1144). In addition, samples 1,137–1,140 were completely dried before the experiment, and the other samples had a pore space water content of 10 to 30 %. The experiments were conducted at pressures from 18 to 30 MPa. The holding time under pressure was from 1 to 2 hours, depending on the permeability.

The study of limestone of group No. 3 with a different composition and higher permeability (average value of 0.038 mD) was carried out on samples 1,180–1,188, of which 1,181 had a moisture content of about 10 %, and the rest – 20–30 %. The study was conducted similarly to the previous one, with an average injection pressure of 18 MPa and a temperature of 120 °C. The holding time under pressure for all samples of the group was 1.5 hours.

After processing, the samples (Fig. 5) were removed from the core holder and extracted in isopropyl alcohol and chloroform.

Fig. 5. Sample of core material after research

After extraction, the samples are dried and their filtration capacity for nitrogen is measured as described above.

5. Results of studies of filtration of acid solution in rocks

5. 1. Effect of methyl acetate on treatment efficiency

Studies of classical stimulation fluids based on hydrochloric and acetic acids (without impurities) showed a complete absence of filtration in the temperature range from 20 to 120 °C at permeabilities of 0.005–0.045 mD and pressure depression up to 30 MPa (Table 1). The reaction takes place on the surface of the carbonate core to form a cavity without penetrating deep into the rock matrix (pore space). The reaction of the rock with hydrochloric acid leads to partial destruction of the rock sample.

Table 1

Studies of classical stimulation fluids (average values)

Composition of core treatment	Initial permeability, μD	Pumped solution, ml	Multiplicity of permeability increase	Notes
8 % HCl+water	5–20	0	0	The solution does not penetrate into the rock matrix, dissolution is superficial with partial destruction of the rock
15 % CH_3COOH+water	15–45	0	0	The solution does not penetrate into the rock matrix, dissolution is superficial

When using methyl acetate-based solutions and in the absence of water in the acid solution, filtration occurs through rock with a permeability of up to 0.001 mD, which is a consequence of low viscosity and surface tension coefficient. Table 2 shows that from 3 to 120 ml of working solution is filtered through the samples, depending on the initial permeability and the operating time of the pumping equipment.

5. 2. Effect of the developed solution on rocks

The effect of the SF-1 solution on carbonate rocks was studied on three groups of rocks with different properties. The results of the part of the study that is most informative for understanding the processes of the solution's influence on the filtration properties of the samples are summarized in Table 2.

Let us consider the results of the study by sample groups:

1) Study of sample group No. 1.

In the study of siltstone with carbonate-clay cement and a high content of iron compounds, a slight decrease in the filtration rate of up to 15 % was observed during solution injection. For example, 120 to 84 cm^3 of solution was pumped through samples 2,134 and 2,135, and immediately after pumping, when the sample contained residual solution and reaction products, the permeability decreased by 30–40 %. After extraction and drying, the permeability increased by an average of 1.35 and 1.47 times, respectively. On average, the absolute permeability increases 1.45 *time*s after pumping about 100 cm^3 of solution.

2) Study of sample group No. 2.

In the study of samples 1,132 and 1,134 (Table 2) with the lowest permeability at pressure drops of up to 30 MPa, the test fluid SF-1 was pumped through the sample for 1.5 hours. At the same time, 8 and 7 cm^3 of fluid were filtered. The sample was purged in the opposite direction with nitrogen (13.3 MPa). After 1 hour, gas began to escape. The initial gas permeability of limestone was 0.0011 and 0.00081 mD. The stimulation fluid was filtered through the core at a rate of up to 5.3 cm^3/hour at a pressure drop of 30 MPa. After extraction, the absolute gas permeability increased to 0.0048 and 0.00102 mD, i. e. 4.36 and 1.26 times, respectively.

Table 2

Results of core studies during filtration of SF-1 solution

Sample No.	ΔP, MPa	Pumped solution, ml	Initial permeability, μD	Permeability after treatment, μD	Permeability increase factor	Notes
1	2	3	4	5	6	7
2,134	20	120	950	1,282	1.35	High content of iron oxides, gradual decrease in filtration during the experiment
2,135	19.2	84	205	302	1.47	Gradual slight decrease in filtration during the experiment, high iron content
1,132	30	8	1.1	4.8	4.36	Water saturation of the sample is 10 %, presence of calcite-mineralized microcracks
1,134	29	7	0.81	1.02	1.26	Water saturation of the sample is 10 %, presence of calcite-mineralized microcracks
1,139	19.5	3.1	1.2	0.35	–3.42	Initially dry sample, no visual cracking
1,140	21	3.5	1.1	0.34	–3.24	Initially dry sample, no visual cracking
1,143	21	5	2.3	4.4	1.91	Water saturation of the sample is 20–30 %, no visual cracking
1,144	18.5	4.8	3.1	14.4	4.64	Water saturation of the sample is 20–30 %, presence of calcite-mineralized microcracks

Continuation of Table 2

1	2	3	4	5	6	7
1,181	18	37.5	41	70	1.71	Water saturation of the sample is 10 %, presence of calcite-mineralized microcracks
1,182	18	34.2	52	227	4.37	Water saturation of the sample is 20–30 %, presence of microcracks
1,183	18	41.5	64	182	2.84	Water saturation of the sample is 20–30 %, presence of calcite-mineralized microcracks
1,184	18	39.3	79	536	6.78	Water saturation of the sample is 20–30 %, presence of microcracks

Note: the effectiveness of treatment with SF-1 solution is highlighted in bold

The study of the initially dried samples (e. g., 1,139 and 1,140 in Table 2) showed a decrease in permeability by an average of 3.3 times, while during the injection period of 1 hour at pressures up to 21 MPa, the smallest amount of fluid filtered through the samples – 3.1 and 3.5 cm^3, respectively (Fig. 6).

The samples moistened to 30 % showed an increase in permeability by an average of 3.5 times (Table 3).

Table 3

General results by sample groups

Sample group	Initial permeability, μD	Final permeability, μD	Average value of treatment efficiency
No. 1	200–950	300–1,450	1.45
No. 2 dried	1.4–1.2	0.3–0.4	–2.9
No. 2 moisture content 10–30 %	1.1–3.1	4–15	3.5
No. 3	40–80	70–640	4.6

3) Study of sample group No. 3.

In the study of carbonate rock of higher permeability, 34 to 42 cm^3 of fluid was filtered through the samples. At the same time, for sample 1,181, which had the lowest moisture content, the permeability increased by 1.71 times, and for samples with a moisture content of 20–30 %, on average, by 4.7 times.

Table 3 and Fig. 7 show the average performance indicators for the three groups of samples.

When analyzing the treatment effectiveness (Fig. 7), it can be seen that the three groups of samples are divided into four groups on the graph, since the second sample group in the absence of water significantly reduces permeability after treatment.

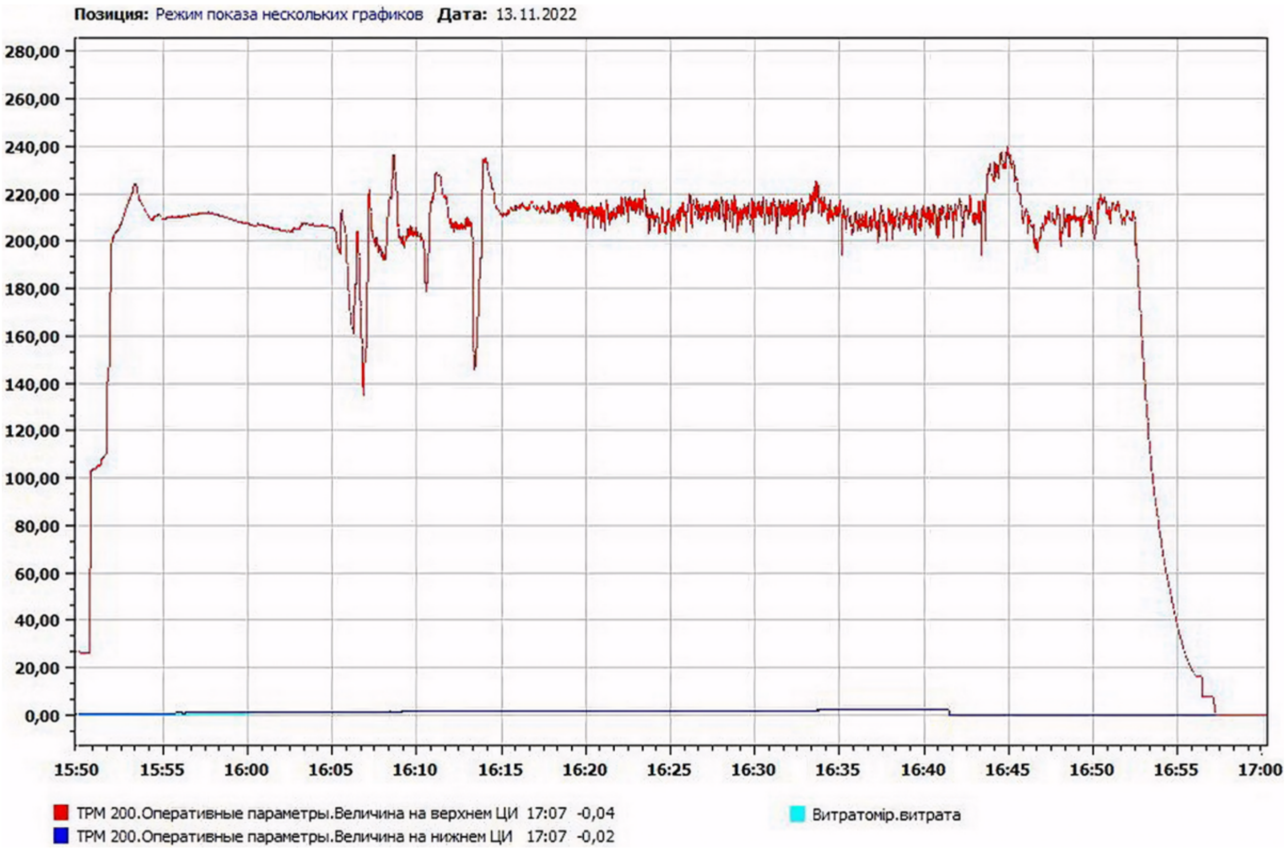


Fig. 6. Process of injection of stimulation fluid over time (sample 1,140)

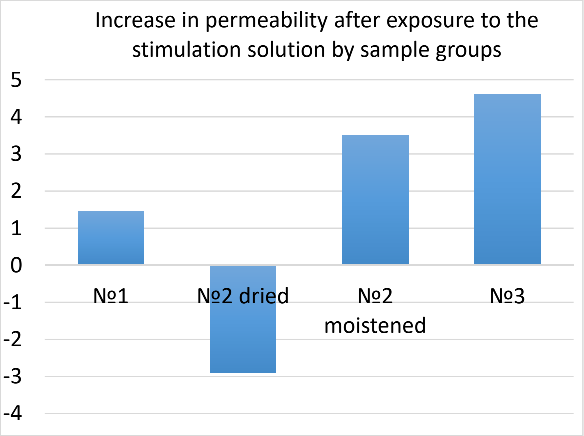


Fig. 7. Efficiency of treatment with SF-1 stimulation solution by sample groups

6. Discussion of the results of studying the effect of acid solutions on carbonate rocks

By analogy with well-known studies [4, 7, 8], we have previously conducted experiments on low-permeability carbonate rocks with classical stimulation fluids – an 8 % aqueous solution of hydrochloric acid and a 15 % aqueous solution of acetic acid (Table 1). The complete absence of filtration is explained by the increased viscosity, rapid reaction of the acid with the rock at high temperatures, due to which the acid loses its activity on the surface of the sample. At the same time, a significant water content in the solution contributes to the development of the dissolution reaction. In real wells, this leads to the formation of cavities in the bottomhole zone or even to the destruction of the reservoir.

The effectiveness of core sample treatment with the developed SF-1 solution largely depends on the permeability, impurity content, and initial moisture content in the pore environment.

The methyl acetate-based solution is highly mobile and does not contain water, which stops the acid from reacting before it comes into contact with the water contained in the pore environment of real rocks. The formation can contain up to 30 % water in various forms, which is a kind of catalyst for the reaction of acetic acid with the rock.

The treatment of siltstone with clay-carbonate cement shows a lower treatment effect (average value +45 %) compared to carbonate rocks, which is explained by the low carbonate content and high content of chemically active compounds, such as iron. In general, the solution is filtered well through this type of rock, and the effect increases with increasing interaction time.

The processing of the sample group No. 2 and No. 3 showed (Table 2, Fig. 7) that the efficiency depends on the microfractures and moisture content of the core. This is due to the fact that the presence of water in the pore space of the rock is important for the reaction and the removal of its products. Thus, when studying dry samples without microcracks with an initial permeability of about 0.001 mD (1,137-1,140), a decrease in permeability of up to 3.3 times after treatment was observed, mainly due to the formation of sediments in the pore space. When filtering through samples with low moisture content (10 %) and with the presence of microcracks (e.g., 1,132, 1,134, 1,181), including those mineralized with calcite, a slight increase in permeability (mainly 1.2–1.7 times) is generally observed. This depends on the crack opening, the degree of mineralization, and the efficiency of sample cleaning after treatment.

When treating carbonates with a water content in the pore space of 20–30 %, an increase in permeability of up to 3 times is observed in the absence of fractures and up to 7 times in the presence of fractures. This is a confirmation of theoretical data on the participation of natural water (including bound water) contained in the pore space and hydrocarbons in the reactions and processes of removal of reaction products. The solution does not lose its chemical activity when in contact with the rock for a long time, which depends on the water content in the pore space (in laboratory conditions up to 2–8 hours).

Some samples immediately after treatment reduce their filtration properties and the effect is observed mainly after extraction of the samples (alcohol, light ethers, chloroform). Such results indicate the precipitation of insoluble compounds due to the low water content in the pore space, which is not enough to dissolve the formed precipitates (e.g., calcium acetate).

Therefore, the limitation of the use of solutions is the water content in the pore space of the rock of less than 10 %, as this can lead to a decrease in permeability due to the precipitation of insoluble compounds. When studying rocks with a permeability of less than 0.001 mD, a rapid decrease in treatment efficiency is observed. The disadvantages of the study include the insufficient effectiveness of solutions with a low carbonate content in the rock and in the presence of a large number of additional chemical compounds.

According to research [12], solutions based on methyl acetate and acetic acid have the lowest reaction rate with the rock, viscosity and surface tension coefficient, which allows solutions to penetrate deeply into the bottomhole zone and create an extensive network of channels. Methyl acetate-based solutions are environmentally friendly compared to other fluids studied. Unlike fast-reacting solutions, which lose their effectiveness at high temperatures near the bottom of the well, the promising methyl acetate-based SF-1 solution reacts with the rock within a few hours. During this time, it is possible to inject an active acid solution into the formation for several meters, even if the permeability of the compacted reservoir is extremely low.

Studies show that methyl acetate is slowly hydrolyzed to methanol and acetic acid in the presence of water in the pore space, which in turn reacts with the rock. This significantly prolongs the reaction time and has a positive effect on the well treatment process.

The development of this study is to introduce additional chemicals into the solution, which will eliminate the existing shortcomings and increase the efficiency in practical application. Depending on the composition of the rock and the fluids that saturate it, it is advisable to introduce gluconic or citric acid, sodium erythorbate, and chelating agents into the developed stimulation solution. The introduction of additional reagents will stabilize possible sediments and neutralize the negative effects of iron compounds, but this requires additional laboratory tests.

7. Conclusions.

1. Methyl acetate, used as a carrier, has the best characteristics among the candidate liquids studied. The main

advantages are low viscosity and surface tension, environmental friendliness, and the ability to additionally release acetic acid due to hydrolysis. The viscosity of the developed solution is less than 0.25 mPa*s at temperatures above 100 °C, which significantly increases the depth of solution penetration into the formation. Due to its low dissociation constant, acetic acid reacts slowly with the rock at high temperatures (compared to strong acids), especially at low water content.

2. The SF-1 solution based on methyl acetate and acetic acid is a promising stimulation solution and is generally recommended for industrial use. Even with an initial permeability of 1.1 μD, 8 ml of the solution was pumped through the sample, which increased the permeability to 4.8 μD, and on average, the solution can increase the permeability of compacted high-temperature carbonate rocks by 3–7 times. The reaction rate of rock dissolution with the studied solution is up to 4 times lower compared to water-based solutions. Retaining its reactivity for a long time, the chemically active solution has the ability to penetrate the rock to a depth of several meters to several tens of meters, depending on the depression and initial permeability of the rock. Studies show that laboratory tests of the effect of solutions on a particular rock are mandatory before industrial use. Reaction processes are significantly influenced by a large number of factors and compounds that cannot be taken into account by calculations or modeling. Water has a significant impact on the reaction and its efficiency. In the complete absence of water in reaction processes, the permeability of samples decreases by 2.9 times. When the water content in the pore medium is 10–30 %, which is close to the natural value, the permeability increases up to 7 times.

Conflict of interest

The authors declare that they have no conflicts of interest in relation to this study, whether financial, personal, authorship, or otherwise, that could affect the study and its results presented in this paper.

Financing

The study was conducted without financial support.

Data availability

Data will be provided upon reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies in the creation of the presented work.

References

1. Vakarchuk, S. H., Dovzhok, T. Ye., Filiushkin, K. K., Hladun, M. V., Maksymchuk, V. A., Kharchenko, M. V. et al. (2014). Perspektyvy osvoiennia resursiv hazu ushchilnenykh porid u Skhidnomu naftohazonosnomu rehioni Ukrainy. Kn. VI. Kyiv: TOV «VTS PRYNT», 208.
2. Vakarchuk, S. H. (2015). Resursnyi potentsial netradytsiynykh vuhlevodniv ushchilnenykh karbonatnykh porid turneiskoho yarusu DDZ. Naftohazova haluz Ukrainy, 5, 46–49. Available at: https://core.ac.uk/download/pdf/73902342.pdf
3. Zimin, O. L., Zezekalo, I. H., Bondar, H. M., Yevdoshchuk, M. I. (2019) Perspektyvy rozrobky ushchilnenykh karbonatnykh kolektoriv u mezhakh Dniprovsko-Donetskoi zapadyny. Naftohazova haluz Ukrainy, 2, 14–18.
4. Kalfayan, L. (2008). Production enhancement with acid stimulation. Tulsa: PennWell, 252.
5. Ruspini, L. C., ren, P. E., Berg, S., Masalmeh, S., Bultreys, T., Taberner, C. et al. (2021). Multiscale Digital Rock Analysis for Complex Rocks. Transport in Porous Media, 139 (2), 301–325. https://doi.org/10.1007/s11242-021-01667-2
6. Mogensen, K., Masalmeh, S. (2020). A review of EOR techniques for carbonate reservoirs in challenging geological settings. Journal of Petroleum Science and Engineering, 195, 107889. https://doi.org/10.1016/j.petrol.2020.107889
7. Palharini Schwalbert, M., Aljawad, M. S., Hill, A. D., Zhu, D. (2020). Decision Criterion for Acid Stimulation Method in Carbonate Reservoirs: Matrix Acidizing or Acid Fracturing? SPE International Conference and Exhibition on Formation Damage Control. https://doi.org/10.2118/199236-ms
8. Yoo, H., Kim, Y., Lee, W., Lee, J. (2018). An experimental study on acid-rock reaction kinetics using dolomite in carbonate acidizing. Journal of Petroleum Science and Engineering, 168, 478–494. https://doi.org/10.1016/j.petrol.2018.05.041
9. Ali, M. T., Nasr-El-Din, H. A. (2020). New Insights into Carbonate Matrix Acidizing Treatments: A Mathematical and Experimental Study. SPE Journal, 25 (03), 1272–1284. https://doi.org/10.2118/200472-pa
10. Rabie, A. I., Nasr-El-Din, H. A. (2015). Effect of Acid Additives on the Reaction of Stimulating Fluids During Acidizing Treatments. SPE North Africa Technical Conference and Exhibition. https://doi.org/10.2118/175827-ms
11. Assem, A. I., Kumar, H. T., Nasr-El-Din, H. A., De Wolf, C. A. (2019). Location and magnitude of formation damage due to iron precipitation during acidizing carbonate rocks. Journal of Petroleum Science and Engineering, 179, 337–354. https://doi.org/10.1016/j.petrol.2019.04.073
12. Zimin, O. (2021). Improvement of acid solutions for stimulation of compacted high-temperature carbonate collectors. Technology Audit and Production Reserves, 6 (3 (62)), 11–14. https://doi.org/10.15587/2706-5448.2021.246604
13. Zezekalo, I. H., Zimin, O. L. (2024). Pat. No. 127806 UA. Sklad dlia obrobky nyzkopronyknoho vysokotemperaturnoho karbonatnoho kolektora pryvybiynoi zony plasta. No. a202005427; declareted: 21.08.2020; published: 10.01.2024, Bul. No. 2. Available at: https://base.uipv.org/searchINV/search.php?action=viewdetails&IdClaim=287611
14. Zimin, O., Zezekalo, I. (2024). Methodology and features of research of filtration properties of compacted deep-seated rocks. Bulletin of the National Technical University “KhPI”. Series: Chemistry, Chemical Technology and Ecology, 1 (11), 17–24. https://doi.org/10.20998/2079-0821.2024.01.03