Acid compositions for enhanced oil recovery from carbonate reservoir

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Abstract. This work is devoted to selection of acidic compositions for use in the process of acid fracturing of carbonate oilfields. The selection is based on the stability of the compositions and their compatibility with oil and corrosion influence on oilfield equipment. The object of research was highly viscous bituminous oil and carbonate rock of Tatarstan Republic (Russian Federation). The object of research was oil and carbonate rock samples from the Vereian horizon of the Vishnevo-Polyanskoe oil field, which is characterized by oil containing in carbonate rocks. The chosen oil can be pertained to highly viscous bituminous oil according to its density and viscosity, what makes the process of its extraction from oil formations complicated. As the result there were selected two acid compositions which contained hydrochloric acid 15 wt\%, demulsifier, dispersant, iron converter (for Fe\textsuperscript{3+} 2000 and 5000 ppm concentration) and corrosion inhibitor. The effectiveness degree of selected compositions was also demonstrated.

1. Introduction

Despite the fact that the International Energy Agency (IEA) affirms that traditional oil reserves will still provide up to 90\% of the global industry up to 2030\cite{1}, the century of light liquid fuel production has passed, and now the expansion of the resource base can be carried out only by development of hard-to-recover oil and gas reserves.

Global recoverable non-traditional oil reserves (heavy oil, natural bitumen and shale, etc.) are about 4.495×10\textsuperscript{8} tons, which almost coincides with the quantity of traditional oil resources; Non-regular extractable gas reserves (coal strata methane, dense sand gas, shale gas and gas hydrate, etc.) are about 4.000×10\textsuperscript{12} m\textsuperscript{3}, which is approximately eight times higher than regular gas reserves\cite{2}. The share of recoverable oil and gas reserves of the whole
world, contained in carbonate reservoirs, is evaluated by experts at a rate of 50-60 %. A large number of huge fields of carbonate type has a prospect of development for the next 50 years. There is nothing surprising that scientists all over the world are interested in the development of carbonate reservoirs. Specialists in the sphere of oil and gas extraction emphasize the complexity of developing carbonate deposits in comparison with siliciclastic deposits. Despite the large number of complex siliceous-clastic reservoirs, carbonate deposits require the development of a new fundamental base for their effective mastering [3].

The main characteristics of carbonate rocks are porosity and permeability. When the rock contains different types of grains and is crushed by stress and deformation, the pore structure become very complex. Often for convenience, porous space is presented as porous bodies that connect with other pores with the help of the necks [4].

The authors of articles [5-7] give several effective and promising ways of developing carbonate reservoirs. Among them, flooding with slightly saline solutions, water and gas impact, pressurizing foam into the reservoir, pumping carbon dioxide into the reservoir, saturation with surfactants, equalizing the rate of intake capacity, increasing the degree of oil extraction by microbiological methods, gravity drainage during steam injection, "smart flooding" [8], concomitant [9] and fracturing.

The meaning of the acid fracturing is to create a pressure at the bottom of the oil well that is higher than the geostatic pressure. The volume of productive stratum is torn along the planes of the minimum stresses of the rock pressure when the liquid is pumped into the reservoir and is accompanied by the fracture splits. After creating a non-natural fracture, the acid is pumped into the reservoir under the pressure, which is greater than the opening pressure of the crack. The acid interacts with the rock on the surface of the split, what leads to appearance of a heterogeneous rough surface. Therefore, after the excess pressure is removed, the interconnected gaps remain in the crack. The result of the acid fracturing is a significant increase of the permeability of the bottomhole stratum zone, which in turn causes an increase the productivity of the oil well, as well as the oil recovery coefficient as a result of the increased drainage zone.

Another important direction of the development of carbonate reservoirs is the selection of acid compositions for treatment, which are an important part of the acid fracturing. The research [10] was also carried out on carbonate rock samples with a permeability of 50-120 mD. For surfactant concentrations selection, hydrochloric acid with a concentration of 15 % by weight was used as the basis compound of the composition. As a result, it was found that the injection speed of acid is the main factor for characterizing the zone being impacted by the composition. It is also known to use emulsified liquids containing acids for treating underground formations. Emulsified acids result a reduced or slowed reaction rate of the acid under the influence of the external oil phase.

2. Methodology
The object of research was oil and carbonate rock samples from the Vereian horizon of the Vishnevo-Polyanskoe oil field. Oil characteristics: density at 20 °C - 0.9058 g/cm³, kinematic
viscosity at 20°C - 155.7 mm²/s. Fractional yield (IBP - 200 °C) - 12.4 %vol. The analyzed oil can be pertained to highly viscous bituminous oil, which makes the process of its extraction from oil formations complicated.

According to the data given in [11], the carbonate rock of the Vereian horizon is characterized by a porosity of 15.5 % and a permeability of 0.055 mm².

The following substances were chosen as additives: corrosion inhibitor, iron converter, demulsifier, dispersant. For the preparation of acidic compositions, the substances were matched in various ratios. Fe³⁺ ions in concentrations of 2000 ppm and 5000 ppm were introduced into the test flasks.

The selection of acid compositions is made according to the appendix to the technological instruction of Rosneft Oil Company in four stages.

Checking the stability of the acid composition. Flasks 1-2 and 4-5 are filled in accordance with Table 1 and placed in a thermostat for 30 minutes to preheat to the bottomhole temperature. This way the stability of the acid composition under conditions of reservoir temperature is determined. Flasks 3, 6 - check flasks, maintained at 20 °C for comparison with four other tests.

| № of flask | Content | Fe³⁺, ppm |
|------------|---------|-----------|
| 1          | 50 ml of composition (HCl 15 %+ all additions) | 0 |
| 2          | 0       | 5000      |
| 3          | 0       | 0         |
| 4          | 0       | 2000      |
| 5          | 0       | 0         |
| 6          | 0       |           |

For compatibility test of active acid composition and oil, the cylinders were filled with required compound in accordance with Table 2.
Table 2. Samples for stability test of active acid composition and oil.

| № of cylinder | Content of test-tube | Content of oil in test-tube by volume, % |
|---------------|----------------------|----------------------------------------|
| 1             | 100 ml (acid composition + oil) | 5000 ppm Fe$^{3+}$                      |
| 2             | 2000 ppm Fe$^{3+}$          | 75                                      |
| 3             | 25                           | 50                                      |
| 5             | 75                           | 25                                      |
| 6             | 50                           | 25                                      |
| 7             | 25                           |                                         |

All test-tubes were placed in thermostat, heated to the bottomhole temperature, for statistic sedimentation no more than 30 minutes. Decantation time being over, samples are checked for phase separation.

If there is no complete separation of the emulsions into two phases or the interface is blurred, then the composition should be changed with selecting the appropriate additive. Content of every test-tube is filtrated through a sieve (100 mesh) to check the presence of clots or sediment.

Compatibility test of partly neutralized acid composition and oil. Acid and calcium carbonate are mixed in quantity according to the Table 3. As chemistry reaction finished, content should be filtrated .The cylinders are filled with oil accordingly data from Table 3, mixture is stirred for 30 s.

Table 3. Samples for compatibility test of partly neutralized acid composition and oil

| № of cylinder | Content of test-tube | Ratio neutralized acid comp.:oil, ml:ml |
|---------------|----------------------|----------------------------------------|
| 4             | 50 ml acid composition + 11.05 g CaCO$_3$ | 5000 ppm Fe$^{3+}$ 44:44 |
| 8             | 2000 ppm Fe$^{3+}$ 45:45 |

Test-flasks 4 and 8 are placed in thermostat for 4 hours, heated to the static bottomhole temperature. Content of every test-tube is filtrated through a sieve (100 mesh) to check the presence of clots or sediment. Test is passed if there is no sediment, emulsion or sedimentation of impurities.

The check for the corrosion activity of the acid composition was estimated by the propagation speed of corrosion through the influence of the acid composition on the sample of pump-compressor tube within 12 hours. The corrosion rate was determined by the change in mass of the sample per unit surface, per unit time:
\[ v = \frac{m_1 - m_2}{S \times t}, \]  
(1)

where \( v \) - corrosion rate, g/(cm\(^2\)×h); \( m_1, m_2 \) - mass of steel sample before and after, g; \( S \) - surface of the sample, cm\(^2\); \( t \) - time of the test, h.

Corrosion rate mustn’t be higher than values from the Table 4.

| Downhole temperature, °C | Corrosion rate, g/cm\(^2\)×h |
|--------------------------|-------------------------------|
| < 93                     | 0.007638                      |
| > 93                     | 0.002010                      |

Effectiveness of acid composition is proved by increasing the coefficient of reservoir permeability using this method: 10 ml of acid composition with the selected concentration were poured into three measuring cylinders and rock samples were placed in for a time (Sample 1 - for 12 hours; Sample 2 - for 18 hours; Sample 3 - for 24 hours).

Porosity after acid influence is calculated with following formula:

\[ \phi_2 = \frac{V_f - V_i}{V_i}, \]  
(2)

where \( \phi_2 \) – porosity of sample after use of acid; \( V_i \) – full volume of the rock sample before use of acid; \( V_f \) - full volume of the rock sample after acid impact.

In order to estimate the changes in the permeability of the reservoir, the following formula is used:

\[ \frac{K_{per1}}{\phi_1} = \frac{K_{per2}}{\phi_2}, \]  
(3)

where \( \phi_1 \) – porosity of carbonate rock sample before use of acid; \( K_{per1} \) – permeability before acid impact; \( K_{per2} \) – permeability after acid impact.

3. Results and Discussions

During the stability test of acid compound in cylinders 1 – 6 separation of mixtures or sedimentation weren’t observed, that indicates the suitability of composition for use according to the method [14]. This suggests that the composition during injection into the well will not cause additional difficulties associated with phase separation and loss of any sediment that can not only settle on the equipment, but also clog the pores of the formation, which in turn is not permissible. Results of oil compatibility test represents us sufficient separation of acid
from oil emulsion (Figure 1), absence of sedimentation after 30 min. heating at the bottomhole temperature, and free pass of substance through the sieve.

![Figure 1](Image)

**Figure 1.** Results of separation “Acid comp.-oil”: a, b, c – Fe$^{3+}$ conc. 5000 ppm; d, e, f – Fe$^{3+}$ conc. 2000 ppm.

Thus, the selected acid composition is completely separated from the oil produced after removing the emulsion from the reservoir. Such kind of composition (1) does not affect crude oil characteristics, what is also confirmed by the free flow of the experimental emulsions through a sieve (without the formation of clots), and (2) does not require additional energy or reagents for the emulsion separation.

Relating the compatibility test for partly neutralized acid and crude oil, it is also possible to note that required degree of separation of test samples 4 and 8 under experimental conditions is achieved (Figure 2).

![Figure 2](Image)

**Figure 2.** Results of emulsion separation «neut. Acid Comp. - Oil»: a – Fe$^{3+}$ conc. 5000 ppm; b – Fe$^{3+}$ conc. 2000 ppm.
It can be concluded that an increase in pH as the result of acid interaction with carbonate rocks does not affect the stability of the emulsion and still allows separating it by settling.

The tests also demonstrated the absence of clots and sediment in experimental mixtures, what eliminates the possibility of blocking the channels of an oil-bearing formation and pumping equipment and does not create complications with the transportation of recovered oil.

Results of corrosion rate test has demonstrated that mass of the sample decreased from 29.30680 g to 29.2893 g. Full square of sample - is 20.0875 cm$^2$. Following calculations use formula (1):

$$ v = \frac{29.30680 - 29.2893}{20.0875 \times 12} = 4.36 \times 10^{-4} \text{ g/(cm}^2\text{xh)} $$

As the bottomhole temperature is lower than 93 ºС, then as a norm of corrosion rate we use maximum corrosion speed value 0.09765 g/cm$^2$ for 12 hours, which is greater than received value, therefore inhibitor of corrosion was chosen correctly.

As result of efficiency test of acid compound for its dissolving properties were estimated following changes (Table 5) in volume of the samples.

| № of sample | Initial volume, V$_i$, ml | Duration of impact, h | Final volume, ml |
|-------------|---------------------------|----------------------|-----------------|
| 1           | 3.0                       | 12                   | 1.8             |
| 2           | 3.0                       | 18                   | 1.8             |
| 3           | 3.0                       | 24                   | 1.5             |

Use formula (2) for approximated calculations of porosity:

a) Sample 1: $\phi_2 = \frac{3.0 - 1.8}{3.0} \times 100 \% = 40 \%$;
b) Sample 2: $\phi_2 = \frac{3.0 - 1.8}{3.0} \times 100 \% = 40 \%$;  
c) Sample 3: $\phi_2 = \frac{3.0 - 1.8}{3.0} \times 100 \% = 50 \%$

Thus, average value of porosity $(40+40+50) / 3 = 43.3 \%$.

Applying formula (3), to measure, how much the permeability of reservoir is increased:

$$ K_{\text{per}2} = \frac{K_{\text{per}1} \cdot \phi_2}{\phi_1} = \frac{0.055 \times 43.3}{15.5} = 0.154 \text{ mcm}^2 $$
Based on obtained data we make a conclusion about efficiency of acid compound, made of HCl 15 %, for acid fracturing and development of Verian reservoir at Vishnevo-Polyanskoe oil field.

In result of all tests two effective for the impact on Vereian reservoir compositions, satisfying the oil compatibility requirements, were chosen for given conc. of Fe$^{3+}$ ions (Table 6).

| Component                  | 5000 ppm Fe$^{3+}$ | 2000 ppm Fe$^{3+}$ |
|----------------------------|--------------------|--------------------|
| HCl aq.solution 15 %      | 98.18              | 98.84              |
| Iron converter             | 1.32               | 0.66               |
| Demulsifier                | 0.20               | 0.20               |
| Dispersant                 | 0.20               | 0.20               |
| Corrosion inhibitor        | 0.10               | 0.10               |

4. Conclusions

In the process of the study was carried out the selection of acidic compositions for use in the process of acid fracturing. The selection was made out through a series of tests aimed at testing the stability of the compositions and their compatibility with oil and corrosion influence on oilfield equipment, the analysis of which was made in advance.

The object of research was oil and carbonate rock samples from the Vereian horizon of the Vishnevo-Polyanskoe oil field, which is characterized by oil containing in carbonate rocks. The chosen oil can be pertained to highly viscous bituminous oil according to its density and viscosity, what makes the process of its extraction from oil formations complicated.

In addition, the choice of the basis of acidic compositions (hydrochloric acid with a concentration of 15 wt %) was justified and its effectiveness was proved for use in the development of a carbonate reservoir. All tasks were performed.

As a result, two hydrochloric acid compositions were selected for use at the stage of acid treatment in the acid fracturing process of the carbonate reservoir of the Vishnevo-Polyanskoe field at a concentration of Fe (III) ions of 2000 and 5000 ppm.

Competent selection of compounds for the acid fracturing simplifies the time-consuming process of carbonate reservoirs development, increases the degree of oil recovery from productive formations, reduces outgoings and increases the economic efficiency of oil production, while enriching the global resource base.

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