Performance of sodium lignosulfonate as thickening additive in compositions for matrix acidizing of bottom hole zone

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Abstract. The work considers one of the promising directions for optimizing matrix acidizing using sodium lignosulfonate as a thickening agent. The mechanism of the interaction of acid solutions containing lignosulfonate with carbonate reservoirs is described. The use of sodium lignosulfonate in acid solutions solves several problems. Slowing the reaction rate allows the acid solution penetrate deeper into the formation, with maintaining the HCl concentration. The increased viscosity of the compositions increases the sweep efficiency of the bottomhole zone in the process of matrix acidizing. These two aspects increase the efficiency of matrix acidizing and the permeability of the bottomhole zone. In the course of this work, the chemical reaction rate of sodium lignosulfonate and hydrochloric acid solutions with carbonate core samples were evaluated. Sodium lignosulfonate in an acid solution reduces the dissolution rate of carbonate samples. It is assumed that slowing down the reaction rate allows the acid solution to form long high permeability channels which increases the efficiency of acidizing.

Key words: viscosity, sodium lignosulfonate, acidizing, reaction rate

1. Introduction
The scope of this work is to develop technology to increase the efficiency of matrix acidizing of the bottomhole zone with using lignosulfonates and improve the technological and economic performance of oil production. The expected results can be used at fields in the Arctic regions of Russia, including the Nenets Autonomous Area which is part of the Arkhangelsk Region.

Due to the high development of the timber and paper industry Arkhangelsk region produces a 20% of paper and cardboard, a third of cellulose production in Russia. [1] Lignosulfonates are by-products of the timber and paper industry. They are successfully used in the production of concrete, drilling fluids, road asphalt, etc. [2, 3].

In scientific and technical sources the possibilities for the use of lignosulfonate solutions as displacing agents in the development of irregular in porosity and permeability, watered formations are considered. [2-5] The increase of oil displacement efficiency is achieved by redistributing filtration flows, isolating water-washed zones with high permeability. The sweep efficiency of low-permeability reservoir zones is increased due to the created pressure gradient, residual oil displacement is provided [2, 4-8].

The article [9] proposes the use of lignosulfonates to inhibit the deposition of surfactants and / or polymer in the formation during flooding. Lignosulfonates are used as viscosifiers in fluids for
selective water shut-off operations. Their use makes it possible to increase the effectiveness of waterflooding at high pressure drops [10].

Lignosulfonates is the generic name for salts of lignosulfonic acid. They are natural water-soluble derivatives of lignin. Lignosulfonates are represented by sodium and calcium salts. They can be found in solutions and also in powder form. Lignosulfonates are classified as anionic surfactants. A sodium lignosulfonate macromolecule forms a non-linear structure similar to globular polymers. Lignosulfonates are economically attractive because they are by-products of cellulose production. [11] The density varies from 1.23 to 1.26 g/ml, depending on the concentration. The acidity of sodium lignosulfonate is relatively low (4.5-5.5 pH) [12].

The patents [13-15] relate to the use of lignosulfonates as ingredients in compositions intended for hydrochloric acid treatment of wells. The high rate of chemical reaction and low permeability of the reservoirs limit the strength and maximum concentration of the acids used. To reduce the rate of reaction with the formation, weak acids or solutions with a low acid concentration are used. However, this does not always lead to an increase in acidizing efficiency. One of the solutions to this problem is the addition of lignosulfonates to hydrochloric acid solutions. In this composition, hydrochloric acid (15%) and sodium lignosulfonate (20%) are used. Lignosulfonate is deposited in the pores and pore channels of the rock, forming a layer that slows down the reaction of the rock with acid. In this way, an optimum response rate is achieved. The optimal reaction rate allows the acid to penetrate deeper into the formation, which has a positive effect on increasing the permeability of the bottomhole zone [16-18].

Thus, lignosulfonates can be used in many technological operations in the oil and gas industry. They have been successfully used as components of drilling fluid for a long time. The direction of acidizing the bottomhole zone with lignosulfonates is very promising due to the high efficiency and low cost of the composition for treatment [18, 19].

The purpose of this work is to study the possibility of using hydrochloric acid solutions with the addition of sodium lignosulfonate for acidizing the bottomhole zone of the well. The first objective is to study the rheological properties of sodium lignosulfonate solutions and hydrochloric acid with the addition of sodium lignosulfonate. The second objective is to assess the reactivity of the studied acid solutions with carbonate core samples on the basis of laboratory studies.

2. Materials and methods

The objects of the research are water solutions of sodium lignosulfonate and hydrochloric acid with the addition of sodium lignosulfonate. The rheological properties of solutions are studied by Brookfield PVS rheometer. The study of the rheological properties of solutions was carried out at temperatures of 80, 60, 40, 20°C. A laboratory water bath was used to maintain the temperature.

At the next stage of the work, the reactivity of acid solutions was studied. Core samples of the same size and weight, cut from one piece were used. The core samples were immersed in acid solutions with different content of lignosulfonate. At regular intervals the mass and size of the samples were measured in accordance with the methodological documentation. The data obtained were used to calculate the reaction rate. During each experiment, the acidity of solutions was constant (pH = 0); the temperature was maintained at 20 °C. The efficiency of sodium lignosulfonate as an inhibitor of the reaction rate was evaluated by the dynamics of the reaction between acid solutions and core samples.

3. Results

3.1 Rheological properties of sodium lignosulfonate water solution (20%)

The sample possesses Newtonian fluid properties at all studied temperatures. The static shear stress is practically zero, the flow curves are linear (Figure 1). The viscosity increases with decreasing temperature and at temperatures of 60, 40, 20°C it increases in comparison with the viscosity at 80°C by 1.5; 2.2; 3.4 times, respectively. The dynamic viscosity of a 20% sodium lignosulfonate solution is shown in Figure 2.
3.2 Rheological properties of sodium lignosulfonate water solution (10%)
The sample possesses Newtonian fluids properties at all study temperatures. The static shear stress is practically zero, the flow curves are linear (Figure 3). The viscosity increases with decreasing temperature and at temperatures of 60, 40, 20°C it increases in comparison with the viscosity at 80°C in 1.3; 1.9; 2.8 times, respectively. The dynamic viscosity of a 10% sodium lignosulfonate solution is shown in Figure 4.

3.3 Rheological properties of hydrochloric acid and sodium lignosulfonate solution
For further research in the field of acid treatments the following solutions were prepared: 15% HCl + 10% sodium lignosulfonate; 15% HCl + 5% sodium lignosulfonate; 15% HCl + 2.5% sodium lignosulfonate. The choice of the concentration of hydrochloric acid is due to the fact that such concentration is most often used in various compositions for acid treatments of wells. When the concentration of sodium lignosulfonate in acid solutions is more than 2.5%, a precipitate is formed. A solution of 15% HCl + 2.5% sodium lignosulfonate is homogeneous. The viscosity of the resulting solutions is too low to be examined with a rotational rheometer. Rheological study by capillary viscometer requires a homogeneous solution. Therefore, only the rheological properties of the solution of 15% HCl + 2.5% sodium lignosulfonate were investigated. The acidity of the solution was pH = 0. Table 1 shows the results of the study of rheological properties.
Table 1. Rheological properties of 15% HCl+ 2.5% sodium lignosulfonate.

| Temperature, °C | Density, g/cm³ | Kinematic viscosity, mm²/s | Dynamic viscosity, mPa·s |
|-----------------|---------------|---------------------------|-------------------------|
| 20              | 1.0764        | 1.2460                    | 1.3412                  |
| 40              | 1.0726        | 0.8875                    | 0.9519                  |
| 60              | 1.0650        | 0.6699                    | 0.7134                  |
| 80              | 1.0488        | 0.5340                    | 0.5601                  |

The solution possesses Newtonian fluids properties at all study temperatures. As the temperature rises, the viscosity decreases. Figure 5 shows the Dynamic viscosity dependence on temperature of 15% HCl + 2.5% sodium lignosulfonate.

3.4 Chemical reaction rate of HCl solutions with addition of sodium lignosulfonate

To study the reactivity with carbonate core samples the following solutions were prepared:
1) 15% HCl;
2) 15% HCl + 10% sodium lignosulfonate;
3) 15% HCl + 5% sodium lignosulfonate;
4) 15% HCl + 2.5% sodium lignosulfonate.

Samples of carbonate rock were taken from one of the fields of the Timan-Pechora oil and gas province. The concentration of carbonate substances in core samples was determined by carbon meter KM-04C. Carbonate rock content of samples was 91±1%. Core samples of the same size and weight, cut from one piece, were placed in vessels with acid solutions. During the experiment, mass and size of each sample were measured (Figure 6).

The rate of a chemical reaction was calculated as the ratio of weight loss per unit of surface area per unit of time. The results of assessing the chemical reaction rate are presented in Tables 2–5.
Table 2. Results of the 15% HCl reaction rate study.

| Time, h | Mass, g  | Δ mass, g | Diameter, mm | Length, mm | Surface area, mm² | Reaction rate, kg/(m²•h) |
|---------|----------|-----------|--------------|------------|-------------------|--------------------------|
| 0       | 27.3726  | -         | 29.73        | 14.34      | 1338.671          | 0                        |
| 0.2     | 26.3146  | 1.0580    | 29.55        | 14.26      | 1323.143          | 3.974734                 |
| 0.4     | 24.7381  | 1.5765    | 28.92        | 13.90      | 1262.242          | 6.097738                 |
| 0.7     | 22.4157  | 2.3224    | 28.56        | 13.37      | 1199.000          | 6.290590                 |
| 1       | 20.3025  | 2.1132    | 28.18        | 12.82      | 1134.380          | 6.037592                 |
| 2       | 14.5605  | 5.7420    | 26.76        | 11.14      | 936.054           | 5.546662                 |
| 4       | 7.5769   | 6.9836    | 22.50        | 8.76       | 618.894           | 4.491211                 |
| 24      | 0.3193   | 7.2576    | -            | -          | -                 | -                        |

Table 3. Results of the 15% HCl + 10% sodium lignosulfonate reaction rate study

| Time, h | Mass, g  | Δ mass, g | Diameter, mm | Length, mm | Surface area, mm² | Reaction rate, kg/(m²•h) |
|---------|----------|-----------|--------------|------------|-------------------|--------------------------|
| 0       | 27.4896  | -         | 29.95        | 14.81      | 1392.777          | 0                        |
| 0.2     | 27.2181  | 0.2715    | 29.61        | 14.76      | 1372.317          | 0.981884                 |
| 0.4     | 26.7119  | 0.5062    | 29.57        | 14.71      | 1365.821          | 1.848702                 |
| 0.7     | 25.8097  | 0.9022    | 29.49        | 14.67      | 1358.421          | 2.207831                 |
| 1       | 25.0209  | 0.7888    | 28.95        | 14.55      | 1322.639          | 1.961413                 |
| 2       | 22.6077  | 2.4132    | 28.34        | 14.21      | 1264.514          | 1.865526                 |
| 4       | 19.2701  | 3.3376    | 27.72        | 13.56      | 1180.273          | 1.365190                 |
| 24      | 4.4194   | 14.8507   | 22.93        | 10.52      | 757.4421          | 0.766403                 |

Table 4. Results of the 15% HCl + 5% sodium lignosulfonate reaction rate study

| Time, h | Mass, g  | Δ mass, g | Diameter, mm | Length, mm | Surface area, mm² | Reaction rate, kg/(m²•h) |
|---------|----------|-----------|--------------|------------|-------------------|--------------------------|
| 0       | 24.7708  | -         | 29.75        | 13.42      | 1253.629          | 0                        |
| 0.2     | 24.3961  | 0.3747    | 29.65        | 13.24      | 1232.657          | 1.507067                 |
| 0.4     | 23.6857  | 0.7104    | 29.55        | 13.13      | 1218.293          | 2.898467                 |
| 0.7     | 22.3662  | 1.3195    | 29.24        | 13.01      | 1194.495          | 3.645851                 |
| 1       | 21.3286  | 1.0376    | 29.09        | 12.58      | 1149.090          | 2.951604                 |
| 2       | 18.2331  | 3.0955    | 27.89        | 12.31      | 1078.043          | 2.779807                 |
| 4       | 13.5531  | 4.6801    | 26.94        | 10.78      | 911.897           | 2.351829                 |
| 24      | 2.5021   | 11.0531   | -            | -          | -                 | -                        |
Table 5. Results of the 15% HCl + 2.5% sodium lignosulfonate reaction rate study

| Time, h | Mass, g | Δ mass, g | Diameter, mm | Length, mm | Surface area, mm² | Reaction rate, kg/(m²•h) |
|---------|---------|-----------|--------------|------------|------------------|-------------------------|
| 0       | 26.4595 | -         | 29.81        | 14.05      | 1315.128         | 0                       |
| 0.2     | 26.0266 | 0.4329    | 29.61        | 13.87      | 1289.569         | 1.661998                |
| 0.4     | 25.3241 | 0.7025    | 29.42        | 13.64      | 1260.047         | 2.755317                |
| 0.7     | 23.8401 | 1.4840    | 29.18        | 13.61      | 1247.019         | 3.946180                |
| 1       | 22.5432 | 1.2969    | 28.71        | 13.21      | 1190.874         | 3.546506                |
| 2       | 19.1008 | 3.4424    | 27.51        | 12.31      | 1063.355         | 3.054171                |
| 4       | 14.0923 | 5.0085    | 26.07        | 11.17      | 914.374          | 2.532450                |
| 24      | 2.1346  | 12.0923   | -            | -          | -                | -                       |

Figure 6. Core samples during the experiment.

Figure 7. Core sample №2 after 24-hour reaction with 15% HCl + 10% sodium lignosulfonate.

After a 24-hour study, all samples except № 2 lost their structural integrity, only small particles remained. In test № 2, the high concentration of sodium lignosulfonate significantly slowed down the rate of chemical reaction between acid and carbonate rock (Figure 6). Figure 7 shows this sample placed in 15% HCl+10% sodium lignosulfonate after 24-hour study. Figure 8 shows the rate of a chemical reaction. Figure 9 shows the accumulated weight loss of core samples.
4. Discussion

The values of the chemical reaction rate were at maximum after 0.5 hours then the interaction was characterized by a sharp decrease of rate followed by the slowdown of the process. The most active solution was 15% HCl without the addition of lignosulfonate. The interaction activity of the solutions decreased with an increase of the lignosulfonate concentration. The shape of the reaction rate curve of 15% HCl + 10% sodium lignosulfonate composition is characterized by the smoothed initial increase in the reaction rate.

According to the graphs in Figure 9, the main dissolution of the core samples occurred during the first four hours. The following interaction is characterized by a decrease of reaction rate and rate of weight loss of the samples.

The results obtained show that in the temperature range of 20-80 °C all solutions possess the properties of Newtonian liquids. When the concentration of sodium lignosulfonate in the hydrochloric acid solution is more than 2.5%, a precipitate is formed, which complicates rheological studies using capillary viscometers.

The kinematic viscosity of the tested solutions is comparable to well acidizing fluids viscosity. It is necessary to carry out a complex of filtration experiments for the study of viscosity influence on the process of chemical interaction.

When studying the reactivity, the most significant weight loss of the samples was obtained in the experiment with 15% hydrochloric acid solution without the addition of lignosulfonate. This result was taken as basic. In experiments № 1-3, the effect of sodium lignosulfonate on the dynamics of the chemical reaction between acid and carbonate rock was studied. In other solutions, sodium lignosulfonate slows down the reaction rate and the rate of sample weight loss. The higher the concentration of sodium lignosulfonate, the slower the reaction rate is. This effect is especially evident when studying the composition 15% HCl + 10% sodium lignosulfonate.

The graphs in Figures 8 and 9 show that due the increase of the lignosulfonate content in the solutions, the chemical interaction proceeds more smoothly. It can be assumed that particles of lignosulfonate are deposited on the surface of the samples and inhibit the interaction between acid and carbonate rock.

The limitations of the research are connected with the experiment conditions. The reactivity of the solutions was studied in open vessels at atmospheric pressure. The filtration properties of solutions influenced insignificantly the experiment results. All four samples were cut from a single 100 mm core sample. It is assumed that all samples had the same properties and mineral composition. The solutions interacted only with the surface of the samples. The effectiveness of matrix acidizing depends on the type of dissolution structures formed in a carbonate rock, which is determined by the ratio of the injection rate and the rate of chemical reaction [20]. The next step is to carry out laboratory
experiments simulating the matrix acidizing of carbonate core samples on constant flow installation with the maintenance of reservoir conditions.

5. Conclusion
The study of the rheological properties of sodium lignosulfonate solutions and hydrochloric acid solution with the addition of lignosulfonate was carried out. The rheological properties of the tested solutions correspond to the characteristics of industrial acid compositions for acidizing.

The reactivity study of acid solutions containing sodium lignosulfonate shows the possibility of changing the rate of a chemical reaction with carbonate rock. When the concentration of lignosulfonate in acid solution increases the reaction rate decreases.

The optimal structure in matrix acidizing is a dominant wormhole with the deep dissemination of acid-formed channels in the formation. The type of acid-formed structure depends on the ratio of the injection rate and the rate of chemical reaction. Slowing down the reaction rate allows the acid composition to penetrate deeper into the formation, maintaining the acid capacity and increases the acid treatment efficiency.

Based on the results obtained, the possibility of practical implementation of projects related to the injection of acid solutions with the addition of sodium lignosulfonate for production optimization in oil fields, including the Arctic zone of the Russian Federation, is shown.

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