Comparison of Buffer Effect of Different Acids During Sandstone Acidizing

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Abstract. The most important concern of sandstone matrix acidizing is to increase the formation permeability by removing the silica particles. To accomplish this, the mud acid (HF: HCl) has been utilized successfully for many years to stimulate the sandstone formations, but still it has many complexities. This paper presents the results of laboratory investigations of different acid combinations (HF: HCl, HF: H₃PO₄ and HF: HCOOH). Hydrofluoric acid and fluoboric acid are used to dissolve clays and feldspar. Phosphoric and formic acids are added as a buffer to maintain the pH of the solution; also it allows the maximum penetration of acid into the core sample. Different tests have been performed on the core samples before and after the acidizing to do the comparative study on the buffer effect of these acids. The analysis consists of permeability, porosity, color change and pH value tests. There is more increase in permeability and porosity while less change in pH when phosphoric and formic acids were used compared to mud acid. From these results it has been found that the buffer effect of phosphoric acid and formic acid is better than hydrochloric acid.

1. Introduction

The matrix acidizing is a stimulation technique commonly used to increase the formation permeability. This can be done by injecting different acids into the reservoir; it can dissolve soluble minerals that can be present in the rock. Sandstone acidizing is proved to be an extremely challenging due to various stages of acid injection and reactions of acids with different minerals [1]. These reactions are potentially dangerous and can cause precipitation reactions, which should be avoided because they can cause damage to the formation. Over the years, researchers have developed many acidizing systems for sandstone formation [2-7] to obtain desired results by minimizing the precipitation problems. The three main acid systems developed are: Mineral, Organic (slower reacting – less corrosive) and Powdered (acid sticks).

Retarded acid systems had also been developed in the past to solve precipitation problems related to mud acid but the problems remain the same and some precipitates formed, which are not formed with standard acids. In sandstone acidizing, the role of hydrofluoric acid (HF) is to dissolve aluminosilicates while the role of accompanying acid is to keep the reaction products soluble in the spent acid and to keep the change of pH value at minimum [7]. HF is the only acid, which can dissolve siliceous minerals [8]. Therefore, all the acid combinations that might be used in sandstone matrix acidizing must contain HF acid or its precursors. The ability of these acids to dissolve siliceous particles is due to the presence of fluoride ion. It is the only ion, which can react with the quartz [9-11] but the fast reaction of this ion leads to precipitation reaction. The most probable of precipitation
reactions that may lead to the formation damage and reduction in the permeability and porosity are as following:

- Precipitation of potassium and sodium silicates
- Precipitation of calcium fluoride
- Precipitation of hydrated silica

Therefore, the sandstone acidizing is carried out in three stages to minimize the precipitation reactions as result of different ions present in the formation [12]: Preflush stage, main acid and after flush.

The reaction of HF acid with sandstone formation is very complex and involves several interactions. This is due to the diverse nature of the sandstone formation. The most important and dominant minerals in sandstone are quartz, clays, aluminosilicates and carbonate. The reaction of hydrofluoric acid is fast with clays and feldspar, but slower with quartz. The silica reacts with HF to produce silica tetra-fluoride (SiF₄), which further reacts with HF acid to produce fluosilicic acid (H₂SiF₆). Reactions can be written as follows:

\[
4\text{HF} + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \tag{1}
\]

\[
\text{SiF}_4 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 \tag{2}
\]

Thus, at a low concentration of acid, the reaction reverses itself to regenerate HF and precipitate silica [3]:

\[
\text{H}_2\text{SiF}_6 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 6\text{HF} \tag{3}
\]

Therefore, one of the main purpose of the sandstone acidizing acids is to control the formation of silica during the reaction. This can be done by adding some organic or a mineral acid with essential HF acid in the main acid stage. Therefore, significant progress has been made in this field and numerous research papers have been published. This paper presents the laboratory study of different acid combinations used in the main acid stage of sandstone acidizing. The main objective of this research is to investigate the buffer effect of different acids used in sandstone acidizing. The buffer effect is responsible for permeability change and deep penetration of acid into the sample. There will be less change in the pH value, more change in permeability and more penetration of acid into the core sample if buffer effect is good.

2. Experimental Work

The cores were saturated with acid using desiccators by inducing vacuum conditions using a vacuum pump. In a vacuum condition, the acid can penetrate deeper in the samples. Saturation time of 4 hours was allowed to ensure maximum volume of acid to penetrate into the core sample. The core was dried before and after the acidizing process for 24 hours at 80 °C. Total seven core samples were used during experiments mentioned in table 1 (A, B… G). The size of the core is 7.62 cm in length and 3.81 cm in diameter. The total volume used is 175 ml, which includes both acid and distilled water. The volume should be enough to fully immerse the core sample in it [13]. Different acid combinations were prepared as shown in table 1. The chemical composition of each sample was same, i.e., 93% silica, 4% alumina and small quantities of calcium oxide and ferric oxide.

2.1. Saturation of the Sample

- Desiccators and vacuum pump were prepared.
- The sample was immersed in 175 ml of acid solution.
- The lid was placed on the desiccators before the tap was opened.
- Tap was connected to the vacuum pump and opened slowly to evacuate the desiccators.
Tap was closed after achieving a vacuum in desiccators.

The vacuum supply was disconnected and waited for 4 hours to ensure reaction between the core and acid.

The entire step was repeated with all the acid combinations. Different ratios of acids were selected to find the effect of concentration of each acid. A low concentration may not produce best results while a high concentration can cause damage to the formation.

### Table 1. Acid Combinations

| Sr. No | Acid Combination | Mixing % |
|--------|------------------|----------|
| A      | HF: HCl          | 3:12     |
| B      | HF: H₃PO₄       | 3:12     |
| C      | HF: H₂PO₄       | 3:9      |
| D      | HF: H₂PO₄       | 1.5:9    |
| E      | HF: HCOOH       | 3:12     |
| F      | HF: HCOOH       | 3:9      |
| G      | HF: HCOOH       | 1.5:9    |

### 3. Results and Discussion

During acidizing, core samples were allowed to react with different acid combinations mentioned in table 1. After the reaction, different properties of these core samples were measured and analyzed as follows:

#### 3.1. Porosity Measurement

After completing the core-acid reaction, the change of porosity was measured and analyzed using Poro-perm apparatus. The results of porosity (initial and final porosity) are reported in table 2.

- HF: H₃PO₄ is a new combination, which was never used before in the petroleum industry. It is observed an increased in the porosity using acid combinations B, C and D was 44.78%, 75.68% and 55.14% respectively. The results of later two combinations were better than standard mud acid (A), which increased the porosity by 47% only (figure 1).
- HF: HCOOH is known as organic mud acid in petroleum industry. It is observed that acid combinations E, F and G lead to increase the porosity by 40.65%, 50.27% and 53.71% respectively. The results of later two combinations were better than standard mud acid.

### Table 2. Porosity Values

| Sr. No | Acid Combination  | Initial Porosity (%) | Final Porosity (%) |
|--------|-------------------|----------------------|--------------------|
| A      | 3%HF: 12%HCl      | 10.28                | 15.12              |
| B      | 3%HF: 12%H₃PO₄    | 9.89                 | 14.32              |
| C      | 3%HF: 9% H₂PO₄    | 9.17                 | 16.11              |
| D      | 1.5%HF: 9% H₃PO₄  | 10.01                | 15.53              |
| E      | 3%HF: 12%HCOOH    | 10.11                | 14.22              |
| F      | 3%HF: 9%HCOOH     | 10.98                | 16.50              |
| G      | 1.5%HF: 9%HCOOH   | 10.52                | 16.17              |
3.2. Permeability Measurement
Permeability is one of the most important parameters, which controls the flow rate of the oil from the reservoir. It is also measured and analyzed using Poro-perm apparatus. Table 3 shows the results of permeability including (initial and final permeability).

- **HF: H$_3$PO$_4$** is a new combination, which showed a significant result. It is observed an increased in the permeability using acid combinations B, C and D was 68.35%, 110.20% and 46.62% respectively. The result of C is better than standard mud acid, which increased the permeability by 76% (figure 2).

- **HF: HCOOH** also showed significant results. It is observed that acid combinations E, F and G lead to increase permeability by 56.21%, 95.37% and 57.06% respectively. The result of C is better than standard mud acid, which increased the permeability by 76%.

| Sr No | Acid Combination          | Initial Permeability (md) | Final Permeability (md) |
|-------|---------------------------|---------------------------|-------------------------|
| A     | 3%HF: 12%HCl              | 70.26                     | 123.876                 |
| B     | 3%HF: 12%H$_3$PO$_4$      | 71.46                     | 120.305                 |
| C     | 3%HF: 9% H$_3$PO$_4$      | 70.5                      | 148.223                 |
| D     | 1.5%HF: 9% H$_3$PO$_4$    | 72.89                     | 106.868                 |
| E     | 3%HF: 12%HCOOH            | 71.58                     | 112.511                 |
| F     | 3%HF: 9%HCOOH             | 74.36                     | 145.278                 |
| G     | 1.5%HF: 9%HCOOH           | 72.25                     | 113.474                 |

**Figure 1.** Porosity Comparison.
3.3. Color Change Test

The original color of the sample was light gray, but the change in the color was observed when the samples were dried in the oven after acidizing. This change in color was occurring because different reaction products were formed during the reaction.

- **After reaction with HF: HCl:** The change in color of the sample which was reacted with HF: HCl shown in figure 3(a). It indicates that the reaction is very fast and most of the acid reacted with and penetrated into the core at the early stages of reaction. It is clear from the figure 3(a) that some portions of the core remain un-reacted. Therefore, most of the acid used at the start due to very fast reaction of mud acid with the core. This fast reaction is due to the presence of HCl [3].

  ![Figure 3(a). Change in color after reaction with HF: HCl.](image)

- **After reaction with HF: H₃PO₄:** The core reacted with HF: H₃PO₄ is shown in figure 3(b). The main difference between the results of this combination and previous one is the iron content (dark brown color) which is formed by iron precipitate or corrosion products. These components can easily be observed in other reacted core samples. Therefore, it indicates that this acid may not corrode the tubing and other things. Figure 3(b) also shows that the penetration of this acid is at its maximum rate and which leads to a color change throughout the core sample.

![Figure 2. Permeability Comparison.](image)
After reaction with HF: HCOOH: The sample reacted with HF: HCOOH can be seen in (figure 3(c)). It shows that the change in color also darker at the outer edges and some parts of the inner core reacts with the acid. This indicates that the reaction is slow compared to mud acid. This slow reaction is due to presence of organic acid [7].

3.4. pH Value Test
The change of acid solution pH value during acidizing process is very important to determine the extent of acid penetration in the formation. An increase in the permeability and porosity of the core sample also depends on the change in the pH value of acid solution. Moreover, the change in the pH value also gives information about the buffer action of the acid. The HCl contains one hydrogen ion; HCOOH contains two hydrogen ions, while H₃PO₄ contains three hydrogen ions. However, frequent changes in the pH value refer to the fast reaction rate of the acid solution with the core and less penetration. The pH value change was obviously noted when HF: HCl reacted with the core sample reported in table 4. It indicates that most of the acid has been spent due to the fast rate of reaction of acid with the core. Whereas a change in pH value remained less when HF: H₃PO₄ and HF: HCOOH were used which is the indication of the low reaction rate. Figure 4 represents the change in the pH value of each sample. The maximum change (1200%) was observed when mud acid was used, while minimum change (866%) was noted when phosphoric acid has been added. This effect shows that the buffer effect of phosphoric acid was better than HCl acid.
Table 4. pH Values

| Sr No | Acid Combination | Initial pH | Final pH | % Change  |
|-------|------------------|------------|----------|-----------|
| A     | 3%HF: 12%HCl     | 0.023      | 0.32     | 1291.30   |
| B     | 3%HF: 12%H₃PO₄  | 0.033      | 0.39     | 1081.81   |
| C     | 3%HF: 9% H₃PO₄  | 0.036      | 0.37     | 927.777   |
| D     | 1.5%HF: 9% H₃PO₄| 0.040      | 0.44     | 1000      |
| E     | 3%HF: 12%HCOOH  | 0.029      | 0.34     | 1072.41   |
| F     | 3%HF: 9% HCOOH  | 0.030      | 0.29     | 866.667   |
| G     | 1.5%HF: 9% HCOOH| 0.036      | 0.37     | 927.8     |

**Figure 4.** Porosity Comparison.

4. Critical Analysis

The color change test of HF: HCl shows that most of the acid was reacting at the edges and the penetration is not deep because when the reaction is fast; pH value of the solution increases and acidity becomes less. That is why; the permeability and porosity change was also less with mud acid.

The permeability and porosity change by HF: HCOOH and HF: H₃PO₄ was better than mud acid mentioned in Tables 2 & 3 and also the pH value change is less as reported in Table 4. Therefore, maximum penetration can be achieved with these combinations. These results are also supported by the color change test. Therefore, it is concluded that the buffer action of phosphoric (H₃PO₄) and formic acid (HCOOH) is better than hydrochloric acid (HCl).

5. Conclusion

Deep penetration into the formation can be achieved using phosphoric acid in the main stage as compared to standard hydrochloric acid, is good for acidizing perspective. This effect is due to less change in pH value during the acidizing process. The combination of (Hydrofluoric and Phosphoric acid) can be used as a main acid in sandstone acidizing, the most successful combinations are (3% HF: 9% H₃PO₄). The buffer action of phosphoric (H₃PO₄) and formic acid (HCOOH) perform better than hydrochloric acid (HCl).
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