An Effective Acid Combination for Enhanced Properties and Corrosion Control of Acidizing Sandstone Formation

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Abstract. To fulfill the demand of the world energy, more technologies to enhance the recovery of oil production are being developed. Sandstone acidizing has been introduced and it acts as one of the important means to increase oil and gas production. Sandstone acidizing operation generally uses acids, which create or enlarge the flow channels of formation around the wellbore. In sandstone matrix acidizing, acids are injected into the formation at a pressure below the formation fracturing pressure, in which the injected acids react with mineral particles that may restrict the flow of hydrocarbons. Most common combination is Hydrofluoric Acid – Hydrochloric with concentration (3% HF – 12% HCl) known as mud acid. But there are some problems associated with the use of mud acid i.e., corrosion, precipitation. In this paper several new combinations of acids were experimentally screened to identify the most effective combination. The combinations used consist of fluoboric, phosphoric, formic and hydrofluoric acids. Cores were allowed to react with these combinations and results are compared with the mud acid. The parameters, which are analyzed, are Improved Permeability Ratio, strength and mineralogy. The analysis showed that the new acid combination has the potential to be used in sandstone acidizing.

1. Introduction

The permeability of sandstone formation can be increased by applying matrix acidizing operation. To remove the damage in the vicinity of the near wellbore, sandstone acidizing has been applied for many years. The reaction mechanism between the different acids and sandstone rock is still not fully identified and understood. According to different companies 25 to 30% of the sandstone acidizing treatment fails due to lack of understanding [1]. Mud acid (HF:HCl) has been developed and applied on sandstone formation since 1965 [2, 3]. Lake in 1962 [4] studied the effect by varying the concentration of HCl in mud acid to study effects on the carbonate particles. Lake et al. also studied the effect of different HF concentrations during treatments. Different acid combinations have been tried on sandstone formation to solve the problems caused by mud acid such as less penetration, fast spending and precipitation etc. HF acid is the essential constituent of all developed acid because of the presence of fluoride ion (F⁻). This is the only ion discovered so far which can reacts with quartz which resulted in the removal of damage around the wellbore. “Therefore, the goal of acidizing in sandstone formation is to dissolve minerals that present in pores to enhance the formation permeability [5]”.
2. Mechanism of Sandstone Acidizing
Acid soluble minerals present around the wellbore start dissolving in HF acid as soon as acid enters the formation. The reactivity of fluoride ion makes this acid very reactive, that’s why the reaction is very fast and most of the acid spends at early stages \[6, 7\]. To slow down this fast reaction rate, HF acid is mixed with another mineral acid (HCl or HCOOH), which acts as a buffer acid and this buffer effect allows deeper penetration of acid into the formation \[8\]. Sandstone formation does not react with acids like nitric and sulphuric effectively \[2\]. During acidizing with mud acid, the most important concerns are the reaction of carbonates with HF and HCl and HF with silica. The reactions that take place when HF acid enters the formation are \[9, 10\]:

\[
\begin{align*}
4\text{HF} + \text{SiO}_2 & \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} & (1) \\
\text{SiO}_2 + 6\text{HF} & \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} & (2) \\
\text{H}_2\text{SiF}_6 + 4\text{H}_2\text{O} & \rightarrow \text{Si(OH)}_4 + 6\text{HF} & (3)
\end{align*}
\]

Other precipitates formed due to this reaction are:

\[
\begin{align*}
\text{H}_2\text{SiF}_6 + \text{Na}^+ & \rightarrow \text{Na}_2\text{SiF}_6 + \text{H}_2 & (4) \\
\text{H}_2\text{SiF}_6 + \text{K}^+ & \rightarrow \text{K}_2\text{SiF}_6 + \text{H}_2 & (5) \\
2\text{HF} + \text{Ca}^+ & \rightarrow \text{CaF}_2 + \text{H}_2 & (6)
\end{align*}
\]

3. Development of New Acids
To avoid the precipitation of above products, new acid systems and acidizing techniques were developed by different researchers. To avoid the precipitation of K_2SiF_6, Na_2SiF_6, and CaF_2; HCl acid is injected ahead of HF acid to remove the ions of calcium, potassium and sodium \[11\]. To avoid the silica precipitation Si(OH)_4, hydrochloric or formic acid have been added with HF acid. This addition has allowed slower reaction of acid with the formation and also this acid maintains the pH of the reaction products, thus avoiding silica precipitation to some extent \[12\]. Still, no research has been done to change HF acid with some other acids consists of fluoride ion. This paper presents new combinations of acids for main acid stage of sandstone acidizing. One combination consists of HF acid and phosphoric acid in which phosphoric acid is the replacement of HCl acid in mud acid mixture. Second combination consists of fluoboric and formic acid in which fluoboric acid is replacing hydrofluoric acid in organic mud acid mixture. Different tests are performed using this acid and analysis is presented.

4. Experimental Work
Acid saturation was performed on Berea core samples of 3 inch in length and 1.5 inch in diameter at standard temperature and pressure condition. Properties of sandstone core sample are presented below:

- Company: Cleveland Querries
- Weight: 0.9 kg/core
- Effective Porosity: 9 – 10%
- Permeability: 65 – 70%
- Strength: 53.1 MPa
- Mineralogy: 93% quartz, 4.3% clay, 1.75% carbonates, 0.95% iron compounds
- 1.5” Diameter, 3” Length

4.1. Acid Volume Calculation
Volume of acid is calculated using the formula:

\[
M_1V_1 = M_2V_2 \quad (7)
\]

Concentrations of acids are already given by the supplier (acids in liquid form), mentioned in table 1.
Table 1. Acid Combinations

| Sr. No | Acids   | Concentration |
|--------|---------|---------------|
| A      | HCl     | 37%           |
| B      | H₃PO₄  | 100%          |
| C      | HF      | 48%           |
| D      | CH₃COOH| 100%          |
| E      | HCOOH   | 100%          |
| F      | HBF₄    | 50%           |

For example, the calculation for 3%HF: 12% HCl is as follows (Table 2).

Table 2. Acid Volume Calculation

| HF    | HCl     |
|-------|---------|
| \( M_1V_1 = M_2V_2 \) | \( M_1V_1 = M_2V_2 \) |
| \( (48) V_1 = (3) (175) \) | \( (37) V_1 = (12) (175) \) |
| \( V_1 = 10.75 \text{ ml} \) | \( V_1 = 56.75 \text{ ml} \) |

The total amount of solution is 175ml; the remaining volume will be filled in by the distilled water. Volume of water = 175-56.75-10.75= 107.5 ml

4.2. Experimental Setup
Different experiments were performed on the core samples before and after acidizing process. These experiments consist of permeability, strength and FESEM analysis. Figure 1 shows the experimental setup for saturation of core sample.

Figure 1: Core saturation experimental setup

4.3. Saturation of Core Sample
- Prepare the desiccators and vacuum pump.
- Immerse the sample in 175 ml of acid solution.
- Place the lid on the desiccators and open the tap.
- Place this saturation system in appropriate size fume cupboard.
- Connect the tap to the vacuum pump and open the tap slowly to evacuate the desiccators.
- When vacuum is achieved in desiccators, close the tap, disconnect the vacuum supply and wait 4 hours to allow the core to react with the acid.
After saturation, keep the sample in the oven for 24 hours to evaporate the acid present in the sample.

Tests are performed on core sample before and after acidizing process. Figure 2 represents the flow chart of all the experiments performed.

![Flow Diagram of Experiments](image)

**Figure 2**: Flow Diagram of Experiments

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

5.1. Improved Permeability Ratio
The Improved Permeability Ratio (IMPR) is the ratio of the final value of permeability to its initial value. From table 3 and figure 3, it is clear that increase in the permeability when 3%HF: 9% H$_3$PO$_4$ is used gives much better results than mud acid. Increase in permeability is almost 2.5 folds when 3%HF: 9% H$_3$PO$_4$ is applied to sandstone formation while with mud acid the increase is 2 folds. But when HBF$_4$: HCOOH is used all the ratios of acids used show better results than mud acid, which indicates this acid combination is very effective in sandstone acidizing. Therefore, it can be concluded from permeability results that these combinations are better than mud acid.

| Sr. No | Acids            | Initial K | Final K | IMPR  |
|------|------------------|-----------|---------|-------|
| A    | 3%HF: 12%HCl     | 70.26     | 141.76  | 2.01  |
| B    | 3%HF: 12%H$_3$PO$_4$ | 71.46    | 131.47  | 1.83  |
| C    | 3%HF: 9% H$_3$PO$_4$ | 70.5     | 165.90  | 2.35  |
| D    | 1.5%HF: 9% H$_3$PO$_4$ | 72.89    | 115.29  | 1.58  |
| E    | 3%HBF$_4$: 12%HCOOH | 71.81   | 164.96  | 2.29  |
| F    | 3%HBF$_4$: 9%HCOOH | 71.82   | 162.32  | 2.26  |
| G    | 1.5%HBF$_4$: 9%HCOOH | 71.78   | 140.25  | 1.95  |
5.2. Compressive Strength Analysis
To find the compressive strength of the core samples all reacted samples are utilized. The initial value is kept constant as it can be measured only once with an unreacted core sample. The combination (HF: \( \text{H}_3\text{PO}_4 \)), which shows maximum increase in the permeability; it causes change in strength of the core sample about 25% which is almost equal to the result of mud acid. The results are presented in table 4 and figure 4. The strength change with mud acid is also 25% but the change in permeability is less as compare to other acids used. This is due to very fast reaction of the HF acid with the core. Precipitates may forms due to this fast spending of acid which ultimately blocks the pore spaces. This blockage is one of the main cause of less increase in permeability as desired. 3%HBF\(_4\): 12%HCOOH causes the maximum change in strength which is 36%. This combination also leads to more increase in permeability, which indicates that this acid although changes permeability, it is also deteriorating the rock by dissolving the cementing minerals.

![IMPR values](image)

**Table 4. Compressive Strength Values**

| Sr No | Acid Combination       | Initial Peal Load (Mpa) | Final Peak Load (MPa) | % change |
|-------|------------------------|-------------------------|-----------------------|----------|
| A     | 3%HF: 12%HCl           | 53.1                    | 39.6                  | 25.42    |
| B     | 3%HF: 12%H\(_3\)PO\(_4\) | 53.1                    | 42.7                  | 19.59    |
| C     | 3%HF: 9% H\(_3\)PO\(_4\) | 53.1                    | 39.5                  | 25.61    |
| D     | 1.5%HF: 9% H\(_3\)PO\(_4\) | 53.1                    | 41.7                  | 21.47    |
| E     | 3%HBF\(_4\): 12%HCOOH | 53.1                    | 33.7                  | 36.54    |
| F     | 3%HBF\(_4\): 9%HCOOH  | 53.1                    | 38.4                  | 27.68    |
| G     | 1.5%HBF\(_4\): 9%HCOOH | 53.1                    | 47.7                  | 10.17    |
5.3. Mineralogy Estimation

The Field Emission Scanning Electron Microscopy (FESEM) is a versatile, non-destructive technique that reveals detailed information about the morphology and presence of different minerals present in the sample before and after the acidizing operation. The mineralogy changes will indicate that which combination is dissolving more minerals. Mainly two tests are performed using FESEM (EDX and Morphology). Details of EDX are illustrated in Table 5. Mineralogy analysis can help in the determination of corrosive nature of the acid which is one of the main theme of this research. From reacted core samples, the cores which were reacted with best ratio of acid combinations were selected for mineralogy test i.e. 3%HF: 12%HCl, 3%HF: 9%H₃PO₄, 3%HBF₄: 12%HCOOH.

Table 5. Mineralogy Values

| Initial composition | After Main Acid Reaction |
|---------------------|-------------------------|
| Elements            | % weight | HF + HCl | HF + H₃PO₄ | HBF₄ + HCOOH |
|---------------------|---------|---------|-----------|-------------|
| 1 Oxygen (O)        | 55.90   | 51.03   | 50.97     | 55.96       |
| 2 Silicon (Si)      | 37.80   | 27.02   | 34.27     | 36.35       |
| 3 Aluminium (Al)    | 2.60    | 1.89    | 2.49      | 2.30        |
| 4 Potassium (K)     | 1.00    | 0.90    | 0.86      | 0.95        |
| 5 Iron (Fe)         | 0.95    | 1.28    | 0.78      | 2.36        |
| 6 Fluorine (F)      | 0.00    | 0.00    | 7.28      | 0.00        |
| 7 Phosphorus (P)    | 0.00    | 0.00    | 1.12      | 0.00        |
| 8 Chlorine (Cl)     | 0.00    | 1.17    | 0.87      | 0.96        |
| 9 Calcium (Ca)      | 1.75    | 0.81    | 1.36      | 1.12        |
| 10 Carbon (C)       | 0.00    | 15.92   | 0.00      | 0.00        |
6. Discussion and Analysis
The results based on conducting three tests (permeability, mineralogy, strength) stated that the two combinations 3%HF: 9%H$_3$PO$_4$ and 3% HBF$_4$: 12%HCOOH showed the best results with consistency. The combination 3%HBF$_4$: 9%HCOOH also show better results and values are near to mud acid results. Therefore, the two final best combinations are 3%HF: 9%H$_3$PO$_4$ and 3%HBF$_4$: 12%HCOOH.

When HF: HCl reacted with the core sample, there is a change in the mineralogy where carbon is formed as seen from table 5. The change in permeability is also less when this combination (HF: HCl) is used. Carbon is not formed when core samples reacted with other combinations (HF: H$_3$PO$_4$, HBF$_4$: HCOOH) used in this study. This also indicates that the presence of carbon component may be a reason of less permeability increment when mud acid was used.

Increase in iron components was observed when (HF:HCl and HBF$_4$:HCOOH) are used for acidizing. This indicates that acids are corrosive and corrosion inhibitor during acidizing may be needed when these acids are injected into the well. But when (HF: H$_3$PO$_4$) was applied to sandstone formation, the iron component decreased which, is opposite to other combinations. Thus, corrosion inhibitor in not needed when this new acid combination is used which reduces the cost of operation.

The results of strength tests are also in accordance with the results of permeability. It is observed that the acid which cause more change in permeability also causes more decrease in the compressive strength and vice versa. The maximum amount of silicon has been dissolved when hydrochloric acid was used (HF: HCl) mentioned in Table 5. The minimum amount of silicon has been dissolved when formic acid was used (HBF$_4$: HCOOH) and when phosphoric acid has been used (HF: H$_3$PO$_4$), the results are in between the combinations in which HCl and HCOOH are used. The combinations in which HCOOH is present cause more change in strength of the core compared to other combinations. Mineralogy results reveals that the combinations (HF: H$_3$PO$_4$, HBF$_4$: HCOOH) dissolves less amount of silicon minerals and causes more change in strength of the sample. Therefore, it can be concluded that silicon is not the cementing material of the core samples used in this research.

By considering all the results and analysis it can be demonstrated that HF: H$_3$PO$_4$ is the best combination from all the combinations applied on sandstone formation in this paper. It causes more increase in permeability, less change in strength of the core sample and causes less corrosion of the materials. More increase in permeability is also the indication of more penetration of the acid into the formation which is favorable for acidizing process.

7. Conclusion
The change in permeability due to acidizing is better when hydrochloric acid is replaced by phosphoric acid in main acid stage. Phosphoric acid acts as a buffer acid and reduces the corrosion rate of the pipeline as analyzed from the mineralogy test. This buffer effect is also responsible for more increase in permeability and deep penetration. It can be concluded from this analysis that corrosion inhibitor may not be required when phosphoric acid is used as it acts as a corrosion inhibitor itself.

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