

A Comparative Study of Different Acids used for Sandstone Acid Stimulation: A Literature Review

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Abstract. Matrix acidizing is an effective well stimulation technique, in which acids are injected at a pressure below the formation fracture pressure. The application of sandstone matrix acidizing has been widely used in the oil and gas industry for many decades. The application of mud acid, which is a combination of Hydrofluoric acid and Hydrochloric acid (HF:HCl) in well stimulation, has gained its popularity in improving the porosity and permeability of reservoir formation. In fact, this is driven by the effectiveness of HF in dissolving minerals in sandstone and HCl in controlling precipitation. Nonetheless, high temperature matrix acidizing approach is in growing need since many wells nowadays are producing from much deeper and hotter reservoir, with a temperature higher than 200°F. In such conditions, mud acid causes rapid reaction rates, hence becoming less efficient as the acids are consumed too early. Furthermore, mud acid is hazardous and very corrosive. On the contrary, previous studies had shown that Fluoroboric Acid (HBF₄) and Phosphoric acid (H₃PO₄) offered numerous advantages in comparison to the conventional mud acid. HBF₄ can hydrolyze to form HF whereas H₃PO₄ acts as a buffer acid; which is able to penetrate deeper into the formation before spending. Likewise, both acids cause more increase in the permeability, less change in the strength of core samples and significantly less corrosive. This paper had critically reviewed the experimental works which had been done on different types of acids. The advantages and disadvantages of these acids are evaluated. Therefore, a new acid combination (HBF₄:H₃PO₄) is developed and the future work which can be done on it is proposed.

Keywords: Well stimulation; Sandstone; Matrix acidizing; Mud acid; Fluoroboric acid; High temperature

1. Introduction

In this new era, the energy requirement of the world has increased. In 2020, prediction shows that 40% more energy will be demanded than in the current time [1]. High-temperature reservoir acidizing becomes the main target for new oil and gas reserve exploration [2]. This is because many reservoir condition are at high temperature of 200°F, whereas some even exist at ultra-high temperature of 500°F. Therefore, current technology is less suitable for reservoirs at such conditions. hence, all aspects of acidizing, from corrosion rates to treatment-fluid stability must be improved.

Mud acid (HF-HCl) is the most conventionally used acid in sandstone acid stimulation. However at high temperature of 200°F, mud acid can cause rapid reactions rates. Consequently, this would result



in inefficiency of acidizing treatment because the acids are consumed too fast [2]. Mud acid is also very corrosive. In order to overcome the problems of the conventional mud acid at high temperature, new acid combination was proposed in this paper.

The aim of this paper is to review the state-of-art of the sandstone acid stimulation. The paper evaluated the advantages and disadvantages of different acid being used. Based on the literature review, fluoroboric acid, HBF_4 and phosphoric acid, H_3PO_4 were found to offer more advantages. For instance, HBF_4 can hydrolyse in aqueous form to form HF slowly whereas H_3PO_4 acts as a buffer acid; which allow deeper penetration into the formation. These acids increased the permeability of sandstone matrix and were less corrosive in comparison to mud acid. In this paper, the recommendation of the future work that can be done on the new acid was also suggested.

2. Background

2.1. Introduction to Sandstone Matrix Acidizing

Sandstone (also known as arenite) is a clastic sedimentary rock. It is mainly composed of Silica and Silicate minerals, which include quartz, feldspar, various forms of clay, and in rare cases zeolite [3].

Matrix acidizing is effective in increasing the production rate and reducing the skin of a sandstone reservoir. For many years, acids have been applied to stimulate reservoir rocks by changing their properties. The acid is injected into the formation at injection pressure below the formation fracturing pressure. By injecting the acid, the minerals present in the soluble reservoir formation will be dissolved, thus increasing the rate of fluid flow from the reservoir to the wellbore. The common practice is a combination of Hydrochloric Acid (HCl) - Hydrofluoric Acid (HF) with a composition of 3% HF – 12% HCl [4].

2.2. The Mechanism of Chemical Reaction of Sandstone Matrix Acidizing

Mud acid (HF-HCl) is able to dissolve clay minerals [5]. Acid used to stimulate sandstone formations contains Fluoride Ion (F^-), which is a very reactive ion and is the only ion that reacts with the sand and clay significantly. The reactivity of HF acid with silica makes it unique in sandstone acidizing applications. Other acids such as hydrochloric, nitric and sulphuric acid are unreactive with silica [6]. As HF enters sandstone core, almost all the minerals begin to dissolve, but at different rates depending on the intrinsic rates of heterogeneous reactions and the exposed surface areas. The reacting minerals can be divided into two distinct categories: slow and fast reacting. Quartz tends to act at a slower rate whereas feldspar and clay tend to react at a faster rate.

During sandstone acidizing, the following precipitation reactions take place and may lead to formation damage and reduction in the porosity and permeability [7]:

(i) Precipitation of hydrated silica:



(ii) Precipitation of sodium, Na silicates, potassium, K silicates, and calcium, Ca fluoride:



Sandstone acidizing is a challenging task due to multiple stages of fluids and reaction of these fluids with the minerals in porous media [8]. At high temperatures, these reactions cause precipitation

reactions, which are dangerous as the formation can be damaged. To avoid reactions (1), (2) and (3), HCl or organic acid is used in the main acid stage. To avoid reactions (4), (5) and (6), ammonium chloride or hydrochloric acid is used as a pre-flush ahead of the main acid, which usually contains HF acid.

Typically, sandstone matrix acidizing consists of three stages [9], which are:

1. Pre-flush to dissolve Na, K and Ca ions that will react with the silica to form insoluble silicates.
2. Main-flush to dissolve the silicates, feldspar and clay.
3. After-flush to keep the wettability in its original state and clean the formation.

3. Literature Review of Experimental Studies

In the past, researchers had developed organic acids (Acetic, Formic), and powdered (Sulfamic, Chloroacetic) [10]. The choices of acid used and additives added depend on the reservoir formation characteristics and the intention of the stimulation. There are significant numbers of experimental studies that had been conducted to investigate the performance and effectiveness of different acid combinations in sandstone matrix acidizing. All these studies have been critically reviewed. Hence, the research outcomes have formed a basic framework for the experimental setup in the future work.

3.1. Mud Acid (HF:HCl)

Gomaa et al. in 2013 [11] had carried out core flood test to investigate the effect of different mud acid, HF-HCl ratio on the permeability enhancement of the sandstone core sample at 180°F. Four mud acid combinations (1.9% HF:15% HCl, 2.3% HF:10% HCl, 2.6% HF:5% HCl and 2.8% HF:3% HCl) were tested on the core sample. Based on the result, all four acid combinations can successfully enhance the permeability of the core sample. However, better permeability enhancement result was observed with increasing HF:HCl ratio. At the same time, the injected acid volume was also reduced.

Al-Harthi et al. in 2009 [2] stated that although mud acid was proven to be efficient and had been widely used, nevertheless it still caused rapid reaction rates at high temperature of 200°F. This resulted in inefficiency of acidizing process as the acids were consumed too early. It was undeniable that mud acid is also hazardous and corrosive to wellbore equipment. Therefore, all of these disadvantages should be taken into considerations in the experimental setup in the future as to overcome the research vulnerability. In view of the shortcoming of the mud acid, new acid combination ($\text{HBF}_4\text{:H}_3\text{PO}_4$) is foreseen to be a better choice on the other hand. It is inferred to not only be having better permeability improvement, but also less corrosive.

3.2. Chelating Agents

Ali et al. in 2008 [12] had carried out experimental investigation on the use of low pH solution, Sodium Hydroxyethylethylenediaminetriacetic Acid (Na_3HEDTA) in stimulating a high temperature well in West Africa. This chelating fluid showed a high efficiency in stimulating a high temperature formation by increasing its permeability. In addition, Parkinson et al. in 2010 [13] also performed a different approach in stimulating the production zone of Pinda formation, located in West Africa. This formation was having the bottomhole static temperature (BHST) of 300°F and was multilayered with carbonates. A low pH 4 HEDTA chelant was used as the main stimulation fluid for six producing wells from the formation. The result showed a high effectiveness of the stimulation acid at a high temperature. The production of all six wells had been doubled after the stimulation.

LePage et al. in 2009 [14] studied the reaction of Glutamic Acid N, N-Diacetic Acid (GLDA) with calcites in carbonate formation. Comparisons between GLDA and other chelants like Ethylenediaminetetraacetic Acid (EDTA), Hydroxyethylethylenediaminetriacetic Acid (HEDTA), Nitrilotriacetic Acid (NTA) and Ethanoldiglycine Acid (EDG) are discussed. In short, GLDA is less corrosive than HCl and is effective as HEDTA. Apart from that, Mahmoud et al. in 2011 [15] also used GLDA to investigate its effect on sandstone cores stimulation in which various parameter such as

injection rate, volume of GLDA, temperature, and GLDA initial pH value were investigated. The results revealed that GLDA had a strong ability in chelating calcium, iron, magnesium, and it chelated small amounts of aluminum ions from the sandstone cores. Moreover, it showed that the concentration of GLDA before and after core flood experiment was almost the same and showing a high thermal stability up to 300°F. Nasr-El-Din in 2013 [16] further proved that GLDA has high thermal stability and low corrosion potential. Based on the result, GLDA causes 21% and 84% increase in permeability at 200°F and 300°F respectively in comparison to HCl, which causes 42% reduction in permeability due to iron hydroxide precipitation.

Whereas Feng et al. in 2011 [17] used a high temperature deep penetrating (HTDP) acid in its investigation. A new corrosion inhibitor has been developed, which is a mixture of complex organophosphate hydrolyzed fluoride salts to generate HF and make HTDP acid suitable for formations with high temperatures. The HTDP acid also has much higher quartz solubility in comparison to the mud acid and will reduce precipitation. Rignol et al. in 2015 [18] tested on another chelant-based fluid system (low pH chelant + fluoboric acid, HBF_4) in sandstone stimulation under ultra-high temperature of 375°F. The core flow test and chemical analysis were performed on the core sample. According to the sequential dissolution results, the chelant-based fluid did not result in silica precipitation due to the absent of HCl. It is also highly effective in increasing the permeability of the core. Garcia et al. in 2016 [19] had discussed the advantages of Aminopolycarboxylic Acid (APCA) fluid, which contains 1 – 1.5% of HF acid. It is better than the conventional HF acid that showed ineffectiveness in acidizing sandstone at a high temperature of higher than 300°F due to the presence of sodium and potassium iron precipitation. This APCA/HF* blend fluid had been used in offshore reservoirs and successfully result in production enhancement of 30 to 50% BOPD for more than 12 months.

From the literature, many researchers had performed experimental studies using different chelants, which can be used in high temperature well stimulation. It is highly commendable that many researches had focused on the representativeness of those acids in high temperature wells. These acids have been proven to be very suitable and reliable to be applied and used in practice. However, chelating agents are generally more suitable for heterogeneous carbonates and clay-rich sandstones but less suitable for clean homogeneous sandstones due to the precipitation of silica. It is also very costly in comparison to mud acid, retarded and organic acids. On the contrary, the new acid combination ($\text{HBF}_4\text{:H}_3\text{PO}_4$) can eliminate this problem as it is less corrosive, stable and allow deep penetration due to slow hydrolytic reaction.

3.3. Retarded and Organic Acids

Al-harbi et al. in 2012 [20] performed an experimental work using different organic-HF acid mixtures to stimulate sandstone formations. The precipitations that take place during the reactions and the factors affecting these precipitations are investigated. These acids include Acetic (CH_3COOH)-HF, Formic (HCOOH)-HF and Citric ($\text{C}_6\text{H}_8\text{O}_7$)-HF combinations. The type and amount of precipitate were found to be mainly dependent on solution pH, organic-HF type, and initial free fluoride concentration. Also, the main parameter that is responsible for the aluminum-fluoride precipitation, is F/Al ratio. At a certain point over critical ratio, the aluminum fluoride precipitation took place.

Another experimental work was conducted by Yang et al. in 2012 [21] with a combination of HF-organic acids instead of mud acid to minimize the problems that are related to mud acid. The reaction kinetics and products are analyzed and the study outcome revealed the fact that the reactions depend on the type of minerals present in the core samples. Zhou and Nasr-El-Din in 2013 [22] investigated the performance of single stage sandstone acid system (HF – phosphonic acid) during sandstone acidizing in high temperature formation of 300°F. The effectiveness of low pH 3.8 GLDA, HEDTA and Formic acid, HCOOH in removing carbonate minerals from a sandstone core sample were also

investigated. The results showed that the acid system increases the permeability of Berea sandstone core. In comparison to GLDA and HEDTA, HCOOH is more effective in removing carbonate minerals from Bandera sandstone cores.

Similar experimental study was presented by the same research team, Shafiq et al. in 2015 [23] and Shafiq and Ben Mahmud in 2016 [24] with different acid combinations, replacing conventional mud acid. These include the combinations of (1) Orthophosphoric (H_3PO_4) acid-HF, (2) Fluoboric (HBF_4) acid-HCOOH, and (3) HCOOH-HF. The sandstone core samples are saturated in these acid combinations and analyzed in term of the porosity, permeability, mineralogy and strength. Based on their findings, although all these acid combinations can be used as the main acid in sandstone acidizing, yet the best acid combination is 3% HF: 9% H_3PO_4 . By showing permeability increase of 135.32%, this combination is even better than standard mud acid (3% HF: 12% HCl), which shows permeability increase of 101.76%. However, the experimental condition was only at ambient temperature, which is not representative at real field condition. Hence, it shows a research gap which can be bridged in the future.

Likewise, Zhou and Nasr-El-Din in 2016 [25] had also studied the performance of an alternative to mud acid, which is the phosphonic-based HF acid system. The interaction between the new acid systems with the clay minerals was investigated in term of acid concentration, reaction time and temperature. In comparison to mud acid, phosphonic-based HF acid system shows significantly better performance of permeability enhancement of 177.86% at 300°F.

Therefore, it is clear that there are many different retarded and organic acid combinations, which can be applied in sandstone stimulation apart from the conventional mud acid, which have been widely used. Out of all the acid combinations used and tested experimentally, ($\text{HBF}_4\text{:H}_3\text{PO}_4$) can be further tested from the research conducted by Shafiq and Ben Mahmud in 2016 [24] at the higher temperatures of 80°C and 100°C. Then, these results should be compared with the performance of mud acid at the same temperatures. In conclusion, the experimental procedures and outcomes from these literatures have provided some constructive approaches for the experimental setup and design in the future.

3.4. Comparison of Different Acid Combinations

Table 1. Comparison of Different Acid Combinations used in Matrix Acidizing

Acid Formulae	Authors and Years	Advantages	Disadvantages
Conventional Mud Acid	Al-Harthy et al. (2009) [2], Gomaa et al. (2013) [11]	- HF dissolves minerals in sandstone. - HCl controls precipitation. - Different HF:HCl concentration can successfully improve the permeability of the core.	- Cause rapid reaction rates at high temperature of 200°F. - Inefficiency of acidizing process as the acids are consumed too early. - Hazardous, difficult for safety control and corrosive to wellbore equipment.
Chelating Agents	Ali et al. (2008) [12], LePage et al. (2009) [14], Parkinson et al. (2010) [13], Mahmoud et al.	- Have high thermal stability up to 300°F. - Less corrosive than HCl. - Less corrosive and not hazardous. - Highly effective for heterogeneous carbonate and	- Less suitable for clean sandstone due to the precipitation of silica. - High cost in comparison to other acids.
GLDA			
EDTA			
HEDTA			
NTA			

EGD/HEIDA HTDP APCA	(2011) [15], Feng et al. (2011) [17], Nasr-El-Din (2013) [16], Rignol et al. (2015) [18], Garcia et al. (2016) [19]	clay-rich sandstone. - Successful application in offshore wells, with improved production of 30% - 50% BOPD.	
Retarded and Organic Acids HCOOH CH ₃ COOH HBF ₄ H ₃ PO ₄ C ₆ H ₈ O ₇	Al-harbi et al. (2012) [20], Yang et al. (2012) [21], Zhou and Nasr-El-Din (2013) [22], Shafiq et al. (2015) [23], Shafiq and Ben Mahmud (2016) [24], Zhou and Nasr-El-Din (2016) [25]	- Act as a buffer and able to penetrate into deeper formation before spending. - Stable and not sensitive to undissolved fines. - Less corrosion and slow hydrolytic reaction.	- Reaction Mechanism with sandstone is not investigated up to date. - Less investigation shown at elevated temperatures. - Less practical results in field.

4. Conclusion

In the past, mud acid (HF:HCl) had been well proven for its effectiveness in improving the porosity and permeability of sandstone reservoir formation. This is due to the uniqueness of HF in dissolving silica minerals in sandstone and HCl in controlling precipitation. However, as the well temperature increases to more than 200°F, mud acid faces significant problem like rapid reaction rates, which results in early acid consumption and decreased acidizing efficiency. Mud acid is also hazardous and very corrosive. Therefore, Fluoroboric Acid (HBF₄) and Phosphoric acid (H₃PO₄) has been proposed in the future work as they offered numerous advantages in comparison to the conventional mud acid. Both acids result in more increase in the permeability and significantly less corrosive.

5. Future Work Recommendation

In the future, it is recommended that these two acids can be developed as a new acid combination. The newly acid combination is proposed to be experimentally tested using core flooding equipment at higher temperature at 80°C and 100°C. Different analytical tests such as Poro-Perm, FESEM, CT Scan, ICP and FNMR can be done to investigate the effectiveness of the new acid combination.

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