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New Acid Combination for a Successful Sandstone Acidizing

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Abstract. With the development of new enhanced oil recovery techniques, sandstone acidizing has been introduced and played a pivotal role in the petroleum industry. Different acid combinations have been applied, which react with the formation, dissolve the soluble particles; thus increase the production of hydrocarbons. To solve the problems which occurred using current preflush sandstone acidizing technology (hydrochloric acid); a new acid combination has been developed. Core flooding experiments on sandstone core samples with dimensions 1.5 in. × 3 in. were conducted at a flow rate of 2 cm³/min. A series of hydrochloric-acetic acid mixtures with different ratios were tested under 150°F temperature. The core flooding experiments performed are aimed to dissolve carbonate, sodium, potassium and calcium particles from the core samples. These experiments are followed by few important tests which include, porosity-permeability, pH value, Inductively Coupled Plasma (ICP) analysis and Nuclear Magnetic Resonance (NMR measurements). All the results are compared with the results of conventional hydrochloric acid technology. NMR and porosity analysis concluded that the new acid combination is more effective in creating fresh pore spaces and thus increasing the reservoir permeability. It can be seen from the pore distribution before and after the acidizing. Prior applying acid; the large size of pores appears most frequently in the pore distribution while with the applied acid, it was found that the small pore size is most the predominant of the pore distribution. These results are validated using ICP analysis which shows the effective removal of calcium and other positive ions from the core sample. This study concludes that the combination of acetic-hydrochloric acid can be a potential candidate for the preflush stage of sandstone acidizing at high temperature reservoirs.

1. Introduction

Acidizing is a process in which an unsteady, nonisothermal, 3D flow in porous media cause reaction of minerals and chemicals. Due to the dissolution of rock matrix and reprecipitation of formation products, acidizing can lead to continuous variation in the porosity and permeability of a formation. The main goal of acidizing a sandstone reservoir is to remove the formation damage caused by drilling, completion or production processes [1]. Acidizing can restore the original permeability of the formation or create new pores to increase the permeability.

Three steps are involved when performing acidizing operation for sandstone reservoirs; preflush, main flush and after flush. The mixture of hydrochloric acid (HCl) and hydrofluoric acid (HF), known as mud acid [2, 3] is normally used for the acidizing process to remove the damage around the wellbore. This acid has been applied by [4, 5] and results are compared with other acids. Hydrochloric acid has been applied in the preflush stage to dissolve carbonates and other positive ions [6, 7, 8, 1]. The primary reaction is presented in equation 1 [9]:



However, the success rate of using hydrochloric acid varies during the preflush stage, even damages are reported by field studies during this stage [10]. The preflush problems are mainly caused by the disadvantages of hydrochloric acid. First is the presence of illite which is sensitive to HCl acid, this may cause serious issues by choking the pore throat and thus decreasing the permeability and porosity. Secondly, at high-temperature



conditions, corrosion may occur and also the reaction rate will be high which may cause other problems like precipitation. Thirdly, an ineffective preflush stage may cause secondary and tertiary reaction at later stages of acidizing [9].

Because of so many problems faced using HCl acid, another approach has been studied and used as an alternative to HCl acid in the preflush stage. This new acid system is a combination of hydrochloric and acetic acid, experimented by [11]. The main aim of this study is to overcome the problems related to hydrochloric acid. While the advantages of hydrochloric acid presented by McLeod [12] should be maintained. In this study different methods such porosity and NMR measurements, pH value monitoring, and ICP analysis has been performed to monitor rock and fluid alterations at different stages of acidizing process.

2. Theory

2.1. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) has been widely used in chemistry, physics, and biomedicine and in clinical diagnosis for imaging the internal structure of the human body. The same principle applied in clinical imaging can also be applied for the imaging of fluid-saturated porous rock, such as reservoir rock. "NMR logging is a subcategory of electromagnetic logging [13], that can measure the induced magnet moment of hydrogen nuclei (protons) contained within the fluid-filled pore space of porous media (reservoir rocks)". Conventional logging measurements (e.g., acoustic, density, neutron, and resistivity), respond to both rock matrix and fluid properties and are strongly mineralogy dependent while NMR-logging respond to the presence of hydrogen protons. Information related to the quantities of fluids present, the properties of these fluids, and the sizes of the pores containing these fluids can be obtained using NMR analysis. From this information, it is possible to infer or estimate.

- The volume (porosity) and distribution (permeability) of the rock pore space
- Rock composition
- Type and quantity of fluid hydrocarbons
- Hydrocarbon producibility

2.1.1 BVI determination.

Determination of Bulk volume irreducible (BVI) of water in the rock sample is one of the most widely used applications of NMR logging. BVI represents the immovable or bound water in a formation. BVI is a function of pore-throat size distribution where high threshold pressure due to smaller pore throats retains the fluids in the pores. Figure 1, 2 and 3 explain the different aspects of NMR logging corresponding to T2 time decay (relaxation time).

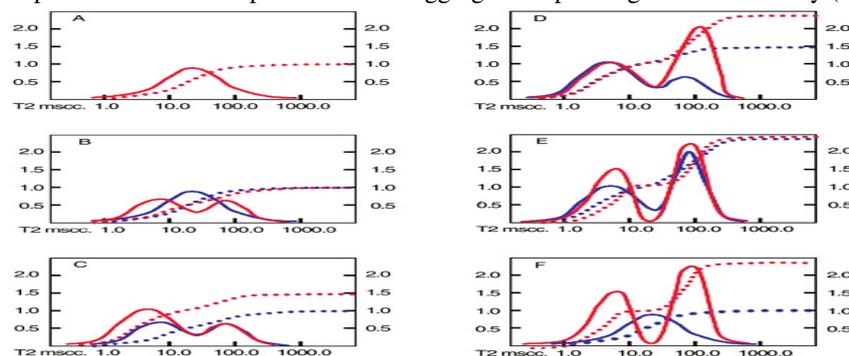


Figure 1. Dependence of T2 distribution on NMR-acquisition parameters. All figures, represents previous results and new results, solid lines represent incremental T2 (read on the left axis), and dashed lines represent cumulative T2 vs. T2 relaxation time (read on the right axis) [13]

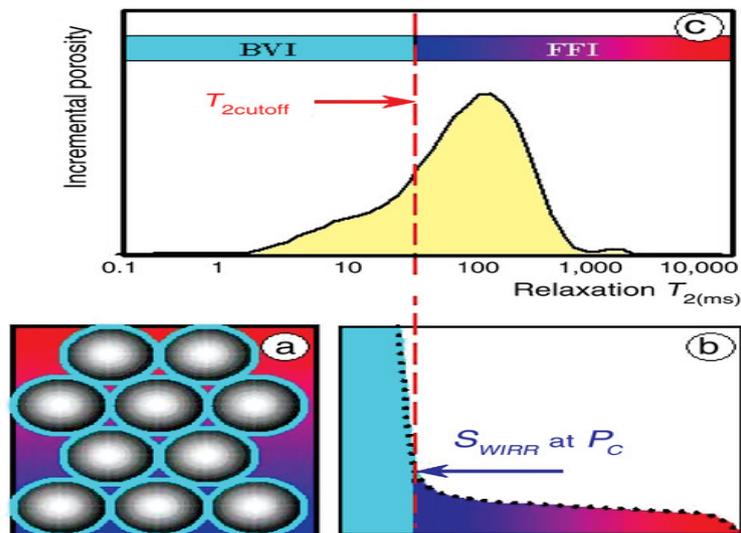


Figure 2. Correlating NMR T2 cutoff to capillary pressure: (a) represents grains, capillary-bound water and free fluids in a gradient tone blue/red; (b) capillary pressure curve (black dots) defines capillary pressure (P_c) in which water saturation becomes irreducible (S_{wirr}); (c) a single-porosity cutoff value on the T2 distribution, corresponding to this pressure [13].

BVI can be used for indicating or estimating permeability and producibility. There are two methods currently used for BVI determination. First one is the cutoff-BVI (CBVI) model, based on a fixed-T2 value ($T_{2cutoff}$) which divides the free-fluid index (FFI) and BVI. The second approach is the spectral BVI (SBVI) model, which assumes the coexistence of free and bound fluids in any pore described by the T2 distribution at water saturation (S_w) = 100% [13]. The SBVI method is used primarily for quantifying movable water and, secondarily, for estimating permeability. This research based on the CBVI model which divides BVI and FFI.

2.1.2 CBVI (cutoff) model.

The T2 signal from the rock matrix is actually very rapid, even modern logging tools cannot detect it. Accordingly, the recorded T2 distribution only represents the porosity occupied by immovable BVI, movable (FFI) water and clay-bound-water (CBW) components. Assuming that the pore size controlled the mobility of reservoir fluids (i.e., the producible fluids reside in large pores and the immobile fluids reside in small pores, a fixed-T2 value can be related directly to a pore size at or below which fluids will not flow. This value ($T_{2cutoff}$) is used to divide the T2 distribution into movable (i.e., producible or free fluids and FFI) and immovable (i.e., bound-fluid, BVI, and CBW) components Figure 3 [14, 15]. T_2 cutoff is a value that may vary from one formation to another and can be affected by lots of factors such as: Capillary pressure, Lithology, Grain size, Compaction, Pore characteristics.

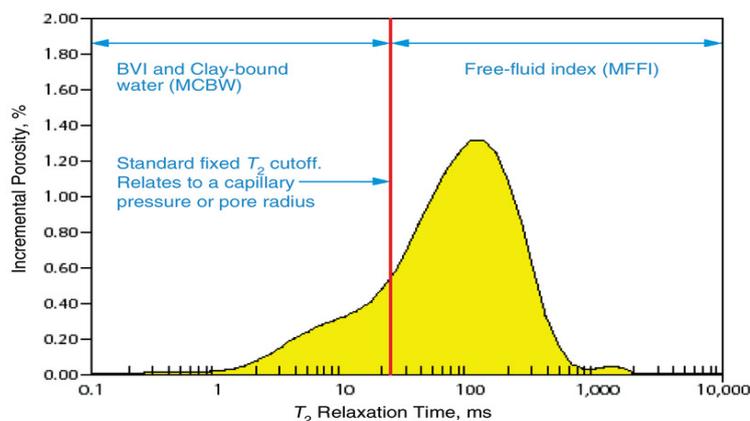


Figure 3. Illustration of the $T_{2cutoff}$ used in the CBVI model to divide NMR porosity into movable and immovable components.

3. Experimental studies

3.1 Materials

Acetic acid and hydrochloric acid were purchased with concentrations of 90-100% and 37% respectively. Berea Sandstone core plugs (1.5× 3 in) were selected for this study. Core samples mineralogy consists of 93% quartz, 5% feldspar and small quantities of other minerals. All the acid solutions were prepared using distilled water prepared in the laboratory.

3.2 Core flood experiments

The core was first dried at 80°F for 24 hours and then was placed in the core holder. After the core was loaded into the core holder, it was put under a confining pressure of 1000 psi using a syringe pump. The injection rate was 2 cm³/min in all experiments. The acid was injected at 150°F until the pressure drop was stabilized. Then the injection was stopped and distilled water was injected again to remove any acid present inside the core sample. The compositions of acids used in all core flood experiments on Berea core samples are listed in Table 1.

Table 1. Sample name and composition

| Sample Name | Composition |
|-------------|------------------------------------|
| Sample A | 15% HCl |
| Sample B | 2.5% CH ₃ COOH: 15% HCl |
| Sample C | 5% CH ₃ COOH: 10% HCl |
| Sample D | 3% CH ₃ COOH: 12% HCl |

4. Result and Analysis

4.1. Porosity Analysis

The porosity is a measure of void spaces in the reservoir and gives information about the storage capacity of the reservoir rock. The porosity is one of the most important parameter for understanding the oil and gas initial in place. Determination of the porosity can be done in many ways i.e., manually and automatically. In this research Automatic Porosity Permeability Apparatus (Figure 4) is used to determine porosity and permeability values. Table 2 characterise the initial and final permeability and porosity values. The initial values are obtained before the core flooding treatment while the final values are recorded after the core flooding.

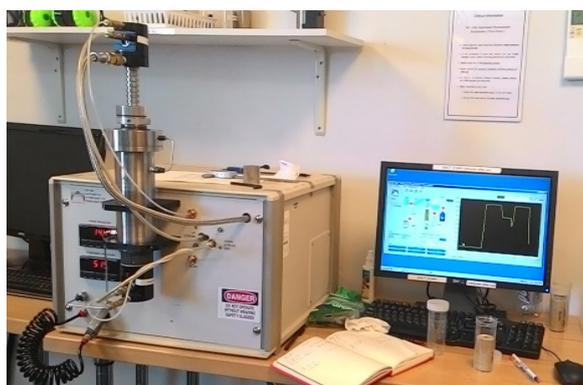


Figure 4. Automatic Porosity permeability apparatus

The main aim of the preflush stage is to remove the calcium, sodium and potassium ions that are present in the core sample. Creating new pores by dissolving these minerals increase the porosity but may have a little effect on the permeability. Therefore, the major objective of using preflush acid is to remove positive ions (Calcium, magnesium, potassium and sodium); and increase the sample porosity. Usually, sandstone samples contain very less amount of sodium, potassium and calcium ions, therefore; as a result, the change in porosity is also less. The

removal of these ions is very necessary in order to get better acidizing results because these minerals can cause precipitation later during the main acid stage.

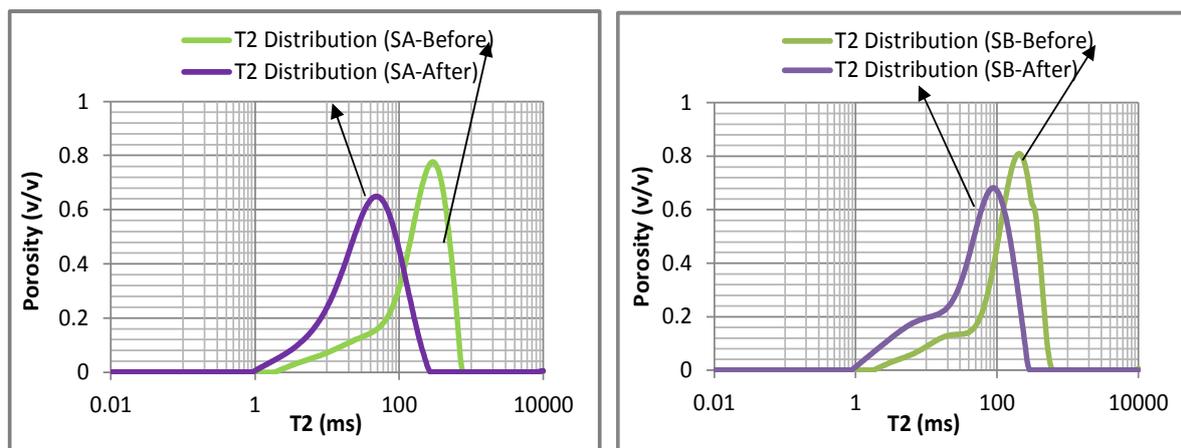
Table 2. Porosity (ϕ) and Permeability (K) results

| Sample Name | Initial ϕ | Final ϕ | % change |
|-------------|----------------|--------------|----------|
| Sample A | 19.567 | 20.613 | 5.34 |
| Sample B | 19.659 | 20.652 | 5.05 |
| Sample C | 19.522 | 20.741 | 6.24 |
| Sample D | 19.038 | 19.925 | 4.65 |
| Sample Name | Initial K | Final K | % change |
| Sample A | 122.76 | 152.16 | 23.94 |
| Sample B | 166.32 | 169.99 | 02.20 |
| Sample C | 113.16 | 113.23 | 00.05 |
| Sample D | 122.76 | 137.49 | 11.99 |

15% HCl is the base case as this is the standard acid used in industry for the pre-flush stage of sandstone acidizing. The permeability increases when 15% HCl was applied is almost 24% as shown in Table 2, while very less variation in permeability has been observed using new acid combinations proposed. The permeability is not the major concern at this stage of acidizing. On the other hand, the porosity results are quite favourable. The change in the porosity when the new combination (5% CH_3COOH : 10% HCl) was applied is 6.2% as shown in Table 2, which is almost 1% more than the base case.

4.2 NMR measurements

NMR measurement has been applied on all four core samples before and after acidizing to investigate the change in pore size distribution using CBVI model. The results can be used to get a better understanding of the change in porosity of each sample after acidizing. Figures 5 and 6 represent the T2 spectrum and cumulative spectrum for each core sample before and after acidizing. Where series 1 (green colour) in each sample represents the initial condition while series 2 (purple colour) is the representative of the reactive sample. The spectrum analysis of each sample is presented in Figure 5 (a, b, c and d) represents that there is a shift in the curve towards the left side. It means that the new small pores have been created and now the relatively smaller pores are dominating the porosity distribution. Although there is an increase in pore space volumes for all samples studied but NMR T₂ distributions indicate that pore sizes decreased for all samples analyzed. The reduction of pore space sizes can be attributed to dissolution of minerals and re-precipitation in larger pores.



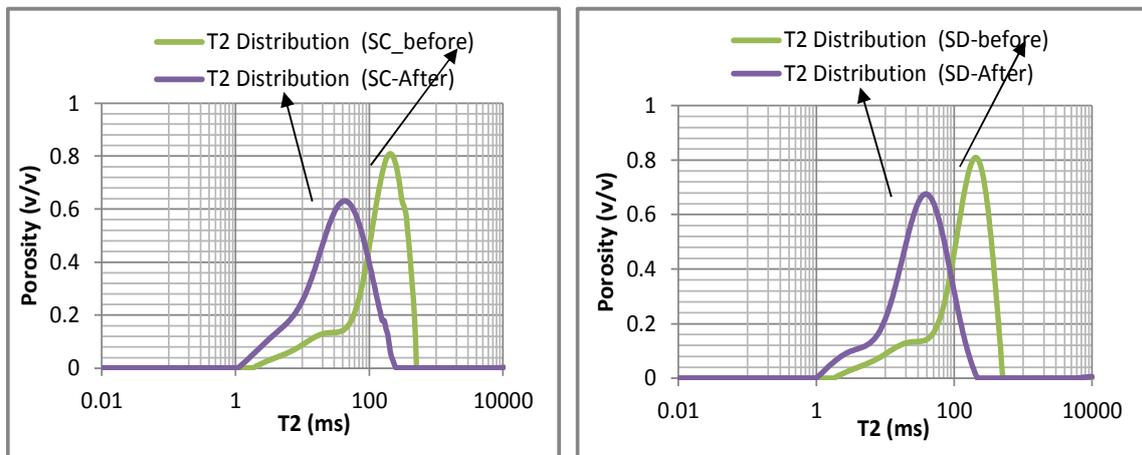


Figure 5. (a) Sample A T_2 spectrum; (b) Sample B T_2 Spectrum; (c) Sample C T_2 spectrum; (d) Sample D T_2 spectrum

The cumulative spectrum Figure 6 (a, b, c, d) clearly represents the increase in the total amount of pores in the sample before and after acidizing with the least change in the cumulative spectrum in sample D (Figure 6d); validating porosity results (Table 2).

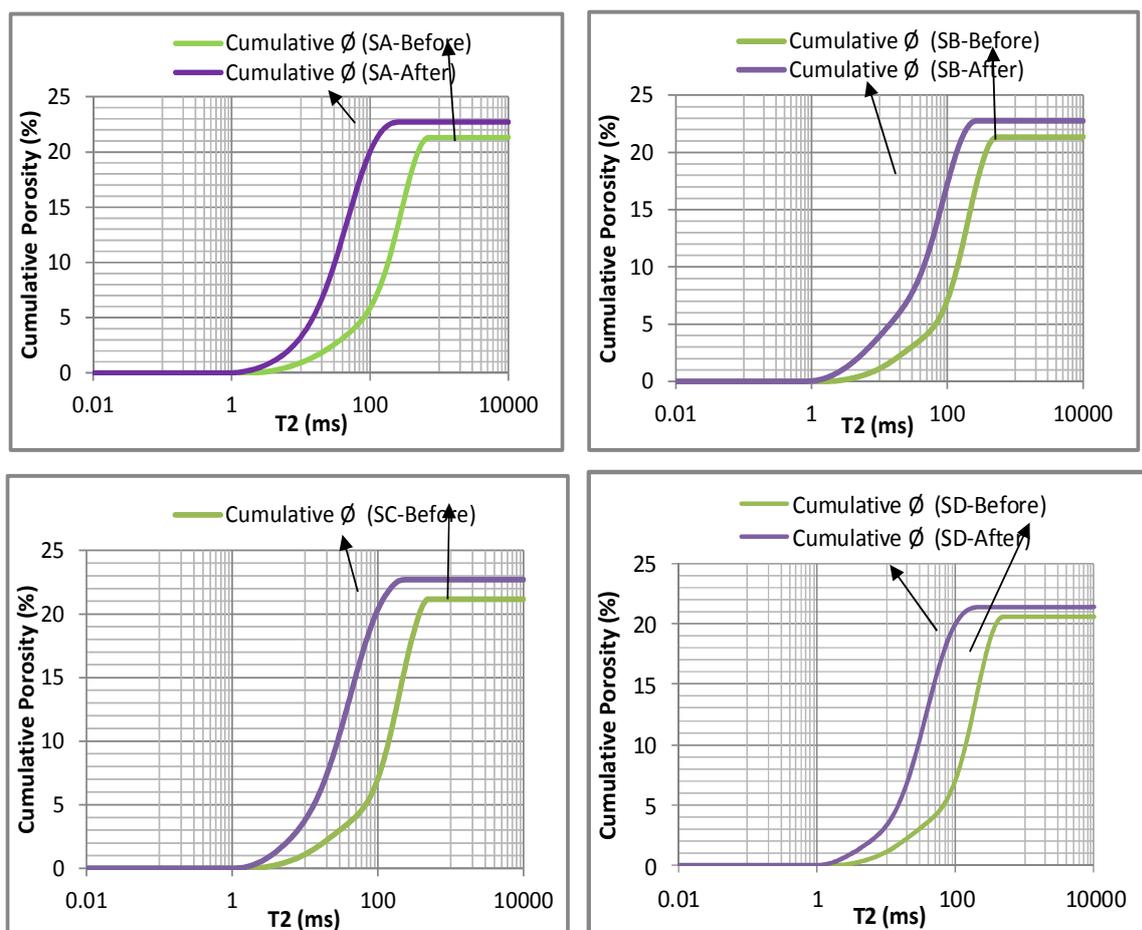


Figure 6. (a) Sample A T_2 commulative spectrum; (b) Sample B T_2 commulative Spectrum; (c) Sample C T_2 commulative spectrum; (d) Sample D T_2 commulative spectrum

Table 3 explains the porosity results obtained from NMR analysis. Figures 5 and 6 are based on these results. These results are validating the porosity results obtained previously mentioned in Table 2; where the maximum change in the porosity is noted within sample C. The advantage of NMR porosity measurement over general porosity measurement is the knowledge of pore distribution which has been explained and analysed using Figures 5 and 6.

Table 3. Porosity Results using NMR.

| Sample Name | Initial ϕ | Final ϕ | % change |
|-------------|----------------|--------------|----------|
| Sample A | 21.31 | 22.71 | 6.57 |
| Sample B | 21.34 | 22.76 | 6.65 |
| Sample C | 21.17 | 22.70 | 7.22 |
| Sample D | 20.59 | 21.40 | 3.94 |

4.3 Inductively Coupled Plasma (ICP) Analysis

ICP analysis is used to validate the porosity results. This test investigates the concentration of different ions dissolved by the acid during the reaction. In this test core effluent samples (reacted acid) were utilized to determine the concentrations of Si, Ca, Na, K, Fe and Mg present in the acid after the reaction. The results presented are in parts per million (ppm). From the analysis presented in Table 4, it can be seen clearly that the maximum amount of each mineral is dissolved when the Concentration (A) is applied. Both samples are collected after 20 minutes of core flood experiments.

Table 4. Concentration of dissolved ions

| Element | Conc (A) (ppm) | Conc (B) (ppm) |
|-------------|----------------|----------------|
| Sodium | 3520 | 2790 |
| Magnesium | 1740 | 1250 |
| Aluminium | 151 | 97.6 |
| Silicon | 144 | 94.8 |
| Phosphorous | 195 | 152 |
| Sulfur | 43.8 | 48 |
| Potassium | 6550 | 6190 |
| Calcium | 6210 | 4340 |
| Titanium | <1.2 | <1.2 |
| Chromium | 18.1 | 8.05 |
| Manganese | 246 | 157 |
| Iron | 4420 | 2690 |
| Cobalt | 2.66 | 1.4 |
| Nickel | 17.2 | 7.12 |
| Copper | 7.19 | 3.2 |
| Zinc | 6.79 | 3.1 |
| Strontium | 5.15 | 5.03 |
| Barium | 3.04 | 2.45 |
| Lead | 6.12 | 4.84 |

where,

Conc (A) = 5% CH₃COOH: 10% HCl

Conc (B) = 15% HCl

The 5% CH₃COOH: 10% HCl can dissolve dissolves 730 ppm of more sodium, 490 ppm of more magnesium, 360 ppm of more potassium, 1870 ppm of more calcium and 1730 ppm of more iron as compared to 15% HCl. The rest of the minerals are not in abundance and their effect on porosity and permeability can be neglected. These results are validating the porosity values mentioned in Table 2, which showed that increase in porosity is more when 5% CH₃COOH: 10% HCl was applied as compared to 15% HCl. To validate ICP analysis results, next step is to analyse the change in the pH values.

4.4 pH Value Test

The pH value determination is also one of the important parameter considered during the acidizing procedure. It determines the buffer effect of acids and can give the idea of penetration power of the acids. More change in pH value describes the fast reaction of acid which subsequently lead to less penetration. Less change in pH value is favourable but it may also indicate no reaction at the late stage because most of the minerals present in the core sample may be consumed during the early stage of reaction and the rest of the acid is coming out without reacting. This may result in the low pH value of the reacted sample. The results of pH value variation for this study are presented in Table 5.

Table 5. pH value before and after reaction

| | Initial pH | Final pH | % change |
|----------|------------|----------|----------|
| Sample A | 0.06 | 0.23 | 283 |
| Sample B | 0.055 | 0.38 | 590 |
| Sample C | 0.09 | 0.41 | 355 |
| Sample D | 0.067 | 0.15 | 123 |

Sample D shows less pH value change as compared to others. This condition is favourable and an indication that the acid coming out can react further deep into the formation. The change in sample C is also almost equal to the change in sample A which is the base case.

5. Conclusion

It can be concluded that the new acid combination (5%CH₃COOH: 10% HCl) had significant effect on the porosity of the core sample and removed positive ions efficiently. It can prove to be a promising aspect in future preflush sandstone acidizing operations. The application of this acid caused more dissolution of carbonates, calcium, magnesium, and sodium ions which ultimately resulted in more increment of the porosity of core sample as compared to the conventional acid.

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