Development of Hybrid Drilling Fluid and Enzyme–Acid Precursor-Based Clean-Up Fluid for Wells Drilled with Calcium Carbonate-Based Drilling Fluids

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ABSTRACT: Significant formation damage can occur during drilling operations because of the invasion of drilling fluid fines and filtrates that lead to pore blocking and saturation alteration mechanisms. This study demonstrates the ways to minimize drilling fluid-related damage and the removal of the deposited filter cake in the carbonate reservoir through judicious selection of bridging particles using "ideal packing theory" and formulation of an enzyme-based clean-up fluid with an acid precursor. The polymer-based drill-in-fluid with a mixed grade of CaCO₃ bridging particles resulted in a compact filter cake with reduced filtration loss preventing internal pore damage significantly. Several ester hydrolysis reaction kinetics were studied, and finally, one combination was chosen as the suitable acid precursor because of its ability to generate a required concentration of acid within the downhole condition. The return permeability of mud-damaged carbonate core plugs was higher than 95% after exposure to the clean-up solution. The corrosion rates were found to be significantly below the industry limits, and the use of acid corrosion inhibitors is eliminated.

1. INTRODUCTION

Drilling fluid typically comprises liquid, gas, or mixture of liquids and solids and is a vital component of oil and gas well drilling operations.¹ Because of the current ongoing challenges in the oil and gas industry, the performance of drilling fluids has become ever more crucial to accomplish the operational objectives. Based on their functions, the drilling fluids are typically categorized into water-based muds, oil-based muds, and gaseous drilling fluids,² followed by more recent modifications in the form of polymer-based³⁴ and nanofluid-based additives.⁵⁻⁷ All drilling fluids perform multiple critical functions during drilling, including hole cleaning and pressure control, maintaining subsurface integrity, and providing power and telemetry for downhole tools.³

Despite the effectiveness of drilling fluids in any rotary drilling operation, there are several aspects that require critical attention and control. One of the major aspects is formation damage (especially in open-hole completions), which refers to the reduction in the natural ability of a reservoir to produce fluids due to a reduction in porosity, permeability, or both. This challenge is typically more pronounced when drilling low permeability and tight formations⁸ and even more for horizontal wellbores.⁹,¹⁰

In particular, drilling fluids with improper particle size distribution result in the plugging of the formation pores.¹¹,¹² Such internal damage causes a decrease in the porosity and permeability of the formation and hence lowers its productivity.

Formation damage is regarded as the root cause of hydrocarbon production loss⁵,¹¹,¹² and is mainly associated with the type of drilling fluids used in relation to the formation type. Davarpanah et al.¹⁴ used a numerical modeling approach to show that when the drilling mud is in contact with the formation for a longer time, the pore throats and fractures would be occupied fast and would cause more serious formation damage rather than their contact for a shorter period. Drilling-related formation damage can be classified into two types. First, internal damage due to the invasion of filtrates and fines that leads to porosity and permeability damage, formation wettability changes, reactions between formation filtrates, precipitation due to filtrates, and the formation of emulsions. Second, external damage that results from deposited filter cake and ineffective filter cake clean-up.¹⁵

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The solid invasion criteria include (1) particles that are much smaller than the average pore throat size, (2) particles that are too large to enter the pores, and (3) particles that are relatively small but forming a bridge (this is the desired range of particle sizes). Thus, the drilling fluid particle size distribution plays a crucial role in internal formation damage of a reservoir.6,17

While all types of drilling fluids cause formation damage, the research in the past decade has shown that drill-in fluids with optimum sized particles can indeed help to minimize the damage.8,12,18,19 Characteristically, a drill-in fluid resembles a completion fluid and is a controlled rheology brine solution containing selected solids of appropriate particle size ranges (salt crystals or calcium carbonate). Specifically, reservoir drill-in fluids are minimally damaging systems designed to drill and complete the reservoir section of the open hole. Drill-in fluids deposit high quality, relatively impermeable filter cake during drilling. This minimizes fluid loss and seals off the reservoir from the wellbore. However, this filter cake also acts as a barrier to the production of reservoir fluid. Thus, it is imperative to remove the filter cake as uniformly as possible to maximize the production rate and net present value of the investment.20 For high permeability formations, a high drawdown may be sufficient to remove the filter cake from the formation face and achieve a reasonable level of clean-up without using chemicals such as filter cake breakers. However, uniform clean-up in medium to low permeability or heterogeneous formations is still a severe challenge.20

Essentially, a well-designed drill-in fluid minimizes the internal damage and allows easy removal of filter cake, which reduces the external damage. The drill-in fluid system can be water-based or invert-emulsion, tailored to a specific completion technique, emphasizing completion compatibility and minimal formation damage. However, the formulation of an effective drill-in fluid is challenging owing to the unique characteristics of the formation under investigation. Fortunately, however, core flood tests on rock core samples assist with a compatible drill-in fluid selection based on formation brine salinity, pH, water hardness, clay mineralogy, and emulsion-forming abilities.

Furthermore, application of ideal packing theory (IPT), which works on Abrams bridging rule, provides the full range of particle size distribution required to quickly bridge the large pore openings, the median pore openings, and smaller pore fractions.21−23 Thus, for drilling fluid to be used as a drill-in fluid, several modifications of the composition and properties must be made. The addition of sized bridging particles such as calcium carbonate and sodium chloride is an example of such modifications. Importantly, some nondamaging additives are added that perform a specific function such as xanthan gum and modified starch. Note that the xanthan gum and starch have been used by a recent investigation to establish rheological filtration properties and to mitigate wellbore instability issues.24 Moreover, the reservoir rock must be characterized for its petro-physical properties [e.g., mercury injection capillary pressure (MICP)] to determine the pore size of the rock core samples6).

Furthermore, the wellbore clean-up is another crucial challenge, and the current research indicates that the clean-up solutions composed of a wide range of components such as strong acids, weak acids, enzymes, chelating agents, and oxidizers are used.25,26 The ability of the clean-up solution to remove the deposited filter cake varies significantly based on its content. Strong acids such as hydrochloric and hydrofluoric acids tend to react with downhole equipment and tubulars, causing severe corrosion, and often result in non-uniform clean-up because of the formation of wormholes. Moreover, reactions, including strong acids, are very fast, resulting in the consumption and tunneling of the acids before a homogenous wellbore clean-up is achieved. Similar issues are observed when utilizing oxidizers and chelating agents, in addition to their inability to dissolve the polymer content in the filter cake.

On the other hand, weak acids (e.g., acetic acid and several other organic acids) have shown an improved cleaning efficiency because of their slow reaction speed, which enables a homogenous removal of the filter cake (the calcium carbonate content). However, weak acids are unable to dissolve the polymer content of the filter cake and are also corrosive to the downhole tools. Moreover, oxidizing breakers are unable to degrade the calcium carbonate content and can react with downhole tubulars. Enzymes (derived from amino acids) are very effective in dissolving starch and xanthan gums but unable to degrade the carbonate content solution. Enzyme and organic acid combinations are also used as a clean-up solution, but it can still cause mild corrosion.

In this work, we established a new wellbore clean-up solution, a combination of enzyme and methyl acetate (MA) ester as acid precursors, for removing damage due to drill-in fluids, especially in low-permeability formations. The MA ester produces weak organic acid and alcohol in the presence of water and is catalyzed by hydrogen ions, thus generating acid in situ by a delayed mechanism using an acid precursor, and implies a fluid free from acid corrosion attack. The in situ generated acid allows uniform distribution along the hole, thus attacking and degrading the carbonate content in filter cake efficiently and uniformly.

While a few studies proposed the application of in situ acid as a clean-up solution,27−29 the current understanding in this context lacks in terms of optimum concentrations of the acid precursor solutions. Moreover, such clean-up solutions have not been rigorously investigated in combination with the widely used drill-in fluids. Nevertheless, it is known that the metal type, temperature, pH, and surrounding environment conditions influence the rate of corrosion. Thus, a corrosion-free breaker chemical would greatly help to mitigate these issues.

Therefore, the two key objectives of this research are (1) to minimize internal damage by formulating a polymer-based drill-in fluid with the appropriate size distribution of bridging particles based on the IPT22 and (2) to remove external damage by formulating a noncorrosive clean-up solution containing enzyme, in situ organic acid precursor, and a catalyst, to obtain a clean wellbore. To accomplish this, a drill-in fluid comprising of xanthan gum and starch-based fluid is formulated with graded calcium carbonate bridging particles applying the IPT. Low to medium permeability carbonate rock samples are selected, which are characterized for their petrophysical properties using routine core analysis. These steps are followed by developing filter cake clean-up fluid comprised of bioengineered modified amylase enzyme and acid precursors (esters) for optimum in situ acid generation potential at wellbore conditions. Clean-up efficiency of the clean-up fluids is measured through high-pressure/high-temperature (HP/HT) filter press experiments. The final conclusions on the efficiency of the designed drill-in fluid and clean-up system are drawn from the core flooding experiments on representative low-permeability carbonate core samples at
reservoir conditions. Finally, the corrosion rates of the proposed clean-up solutions were measured under both static and dynamic conditions. The results of this study contribute to our understanding of advanced clean-up solutions and the associated downhole interactions.

2. MATERIALS AND METHODS

2.1. Formulation of Drilling Fluid with Appropriate Bridging Particles. Preliminary investigation on formulation and optimization of non-damaging drill-in-fluid was conducted using HPHT Filter Press or Permeability Plugging Tester (PPT) that uses ceramic disc as porous media, and the final conclusions were drawn from core-flood studies using field core. Because the pore sizes of the two porous materials are different, the selection of bridging particles was based on their pore size distribution measured differently.

The pore size distribution of the ceramic disks (rated 35 μm and 10 D) was measured through scanning electron microscopy following the published literature. The pore size distribution is shown in Figure 1. The minimum pore size is approximately 10 μm ($D_{10}$), while the median and maximum pore sizes are ~27.5 μm ($D_{50}$) and ~60 μm ($D_{90}$), respectively.

2.2. Core Plugs. A total of five carbonate core plugs were cut from a single core block, acquired from a Middle Eastern carbonate reservoir having nearly homogeneous petrophysical properties. The rock consisted of 96.5% grainstone, 1.4% mudstone, 0.6% packstone, and 1.3% wackestone with 0.2% other minor constituents. The core plugs were subjected to a two-stage cleaning process using toluene in the first stage to remove organic materials, and in the second stage, methanol was used to extract the inorganic salts (API RP-40). This was followed by drying in a hot oven at 95 °C. Subsequently, their petrophysical properties were measured, as presented in Table 1, showing identical samples (due to closely resembling properties).

2.3. MICP Study. MICP test was conducted on core plug #5 (porosity = 15.5% and air permeability = 13.4 mD). The pore throat radius was calculated and plotted against mercury saturation fraction on a semilog graph to indicate the micro, meso, and macropores (Figure 2). The maximum pore size was 71.4 μm ($D_{90}$), which occurred at 1.5 psi, while the median pore size was 9.2 μm ($D_{50}$). Minimum pore size occurred at 55,000 psi corresponding to 0.002 μm ($D_{10}$). Because the sizes <1 μm cannot be sealed by ideal packing, we selected 1.2 μm as the minimum pore size for selecting bridging particle size.

Based on the measured pore sizes of the ceramic discs and core plugs, an optimum blend of bridging particles was determined using commercial software based on IPT. Table 2 shows the dosing and optimum blend of CaCO$_3$ particles in the designed drill-in-fluid, estimated form the above studies.

2.4. Drill-In Fluid Composition and Properties. To validate the bridging particle optimization process, the filtration loss and visible properties of mud-cake and filtrate were evaluated through PPT. Filtration loss was measured for 1 h at 120 °C, applying 200 psi pressure. Five tests were conducted by mixing calcium carbonate powder of different grades (keeping all other ingredients the same). Thickness of the dry cakes was measured using a Vernier caliper. Starch and xanthan polymers and other ingredients to achieve the required properties of a standard drill-in-fluid are shown in Table 3, while the measured properties of the drill-in-fluid are presented in Table 4. Note that there are a variety of drill-in fluids reported in the literature for various applications, which allowed us to select the recipe in Table 3.

| Table 1. Properties of the Carbonate Core Plugs Used |
|-----------------------------------------------|
| sample ID | length (cm) | diameter (cm) | porosity (%) | permeability (mD) |
|----------|-------------|--------------|--------------|-------------------|
| core-1   | 6.44        | 3.83         | 16.4         | 14.6              |
| core-2   | 6.52        | 3.82         | 14.9         | 12.9              |
| core-3   | 7.09        | 3.81         | 15.7         | 13.7              |
| core-4   | 6.75        | 3.82         | 16.1         | 13.9              |
| core-5   | 5.56        | 3.82         | 15.5         | 13.4              |

Figure 1. (a) Cumulative pore size and (b) pore size distribution of 35 μm ceramic disks.

Figure 2. Pore size distribution of the core sample from MICP test.
Table 3. Composition of Drill-In Fluid

| additive          | primary function          | concentration     |
|-------------------|---------------------------|-------------------|
| xanthan gum       | viscosifier               | 3 g/L             |
| modified starch   | fluid loss control        | 20 g/L            |
| calcium carbonate | bridging agent            | function of pore size distribution |
| sodium chloride   | weighing agent            | 250 g/L           |
| magnesium oxide   | pH controller              | 0.5 g/L           |
| lubricant         | lubrication               | 1% by volume      |
| oxygen scavenger  | corrosion inhibitor        | 0.25% by volume   |
| biocide           | bacterial growth          | 1% by volume      |

Table 4. Measured Properties of the Final Drill-In Fluid Formulation

| property          | Unit        | measured value | method/instrument |
|-------------------|-------------|----------------|-------------------|
| density           | lbm/gal (ppg) | 10             | mud balance       |
| viscosity         | s/quart     | 46             | Marsh funnel      |
| yield point       | lbf/100 ft² | 23             | Fann viscometer   |
| plastic viscosity | Cps         | 18             | Fann viscometer   |
| 10 s gel strength | lbf/100 sq ft | 4             | Fann viscometer   |
| 10 min gel strength | lbf/100 sq ft | 15             | Fann viscometer   |
| filter loss       | cm³/30 min/100 psi | 5             | API Filter Press  |

2.5. Clean-Up Fluid. The mud-cake clean-up fluid was prepared by using a modified α-amylase enzyme to degrade the polymeric matrix and a mild acid to react with the calcium carbonate bridging particles.28 Several concentrations of acetic acid in situ, using an acid precursor, was prepared and tested (via core flooding) so that the tubing system used to pump the fluid can be prevented from acid exposure and corrosion. Three different clean-up fluid concentrations of varying quantities of enzyme, acetic acid, and ester were used, and these were (1) 5% enzyme + 3% acetic acid, (2) 5% enzyme + 15% MA ester + 0.5% acetic acid, and (3) 5% enzyme + 15% MA ester + 0.25% acetic acid.

The effectiveness of acid-precursor-based clean up fluid was evaluated using PPT and ceramic discs as porous media. Clean-up efficiency was compared with conventional acetic acid-based clean-up solution, and the optimum catalyst concentration was determined based on residual mud cake. Test-1 was conducted to determine the efficiency of the clean-up solution containing 5% enzyme and 3% acetic acid, while test-2 was conducted using a solution containing 5% enzyme, 15% MA ester, and 0.5% acetic acid and test-3 were conducted using a solution containing 5% enzyme, 15% MA ester, and 0.25% acetic acid. An overbalance of 200 psi and a temperature of 120 °C were maintained for all tests. The cake deposition was allowed for 1 h, and the given exposure time for the clean-up treatment was for 6 h.

Filter cake clean-up efficiency %

\[
\text{Filter cake clean-up efficiency} \% = \left(100 - \frac{\text{weight of remaining filter cake}}{\text{weight of the control filter cake}}\right) \times 100
\]

2.6. Acid Precursors and In Situ Acid Generation Capacity. It is understood from the literature that MA and ethylene glycol diacetate (EGD) concentrations can be altered for efficient acetic acid production at wellbore conditions.30

Thus, these two esters were tested at 120 °C for their efficiency as acid precursors, with the aid of very low concentrations (≤0.5%) of acetic acid as a catalyst. Solutions containing 5–15 wt% esters were hydrolyzed inside an autoclave, and the produced acetic acid concentration was measured intermittently collecting a small aliquot.

2.7. Enzyme. We developed and used high-temperature and organic acid-tolerant α-amylase enzyme, prepared using “directed mutagenesis” and “protein engineering” tools, to minimize denaturation at high temperatures and the underlying chemistry. The detail can be found elsewhere.30 Current research has shown that with suitable modification of its macro-structure, α-amylase enzymes can achieve high temperature tolerance and maximum dissolution of the residual polymers (starch and xanthan) in the mud cake and thus disrupts the filter cake for the acid to attack uniformly.30,34 The hydrolysis of a biopolymer by this enzyme system progresses sequentially, leading to synergistic complex formation with the substrate and rendering it suitable for hydrolysis.35,36 Enzyme solution (5 vol %) was prepared in 2 wt % KCl solution, and thermal stability was evaluated at 120 °C, using high-pressure/high temperature (HP/HT) cells, incubated for 4–12 h. This was followed by visual inspections at regular intervals for any physical change or coagulation following the method described elsewhere.37 Slight cloudiness was observed after 8 h of thermal exposure; however, no coagulation was observed. The final composition of clean solutions is presented in Table 5.

Table 5. Composition of the Clean-Up Fluid

| component         | function                        | concentration (v/v) (%) |
|-------------------|---------------------------------|------------------------|
| enzyme            | accelerates hydrolysis of xanthan and starch | 5                     |
| MA ester          | acetic acid precursor            | 15                    |
| acetic acid       | catalyst                         | 0.25 or 0.5            |

2.8. Clean Up Fluid Efficiency. 2.8.1. Core Flooding Tests to Evaluate Drill-In and Breaker Fluid Efficiency. Temco CFS-830-10000-HC core flooding set-up was used for this purpose with required modifications and adjustments so that the fluids can be pumped either in the forward direction to simulate down-hole circulating and injection conditions or from the reverse direction to simulate production through the formation. The operating temperature and confining pressure were 120 °C and 500 psig, respectively, with a back pressure of 100 psi. Synthetic reservoir brine was used to assess the initial and residual damages. Four core flooding tests were conducted in duplicate with two breaker fluid compositions, as shown in Table 6. The stepwise procedure was as follows:

- Step-1: Permeability measurements from the backward (or production) direction using synthetic brine (at 0.5 mL/min) to assess initial brine permeability.

Table 6. Details of Tests with Treatment Fluid Composition

| test # | sample ID | breaker fluid composition |
|--------|-----------|---------------------------|
| 1      | core-1    | enzyme-5%, MA-15%, surfactant-1%, catalyst-0.25% |
| 2      | core-2    | same as test 1            |
| 3      | core-3    | enzyme-5%, MA-15%, surfactant-1%, catalyst-0.5% |
| 4      | core-4    | same as test 3            |
| 5      | core-5    | used for MICP test only   |
• Step-2: Circulation of drill-in fluid at the core face for 2 h and static exposure for 6 h under 200 psig overpressure to create filter cake.
• Step-3: Measurement of injection and production permeability from the forward and backward direction to evaluate the formation damage caused by the drilling fluid.
• Step-4: Circulation of synthetic brine at a high flow rate (100 cm²/min) followed by treatment with clean-up fluid with a 6 h exposure.
• Step-5: Repeat measurement of injection and production permeability from the forward and backward direction to evaluate the residual damage and the efficiency of the clean-up fluid.

2.9. Corrosion Tests under Static and Dynamic Conditions. Corrosion tests were performed to determine the corrosion rates of the proposed clean-up solutions using potentiostat. Corrosion rates of acetic acid samples, as well as hydrolyzed and non-hydrolyzed MA and HCl samples, were measured under static conditions. The samples were mixed with 50 ppm of oxygen scavenger to eliminate the possibilities of areal corrosion. The tests were conducted at five temperatures (24.8, 40, 55, 70, and 85 °C), and the results were extrapolated to 120 °C. These tests were done using a potentiostat. Samples were picked during the hydrolysis process (at 120 °C) at 2 h interval from 2nd until 12th hour of the ester hydrolysis process with known acetic acid concentration (as shown in Figure 3 below). Corrosion rates for the same samples were also measured through the weight loss method using coupons cut from a piece of production tubing at ambient temperature (24.8 °C).

3. RESULTS AND DISCUSSION

3.1. Impact of Bridging Particles on Filtration Loss and Cake Thickness. To validate the bridging particle optimization process, the filtration loss and visible properties of mud-cake and filtrate were evaluated through PPT apparatus. Table 7 presents the results of the filtrate loss, filtrate quality, and approximate cake thickness.

It is evident that the mixed grade bridging particle (as per IPT) produced 19.3–45.4% less filtration loss and 31.6–58.1% thinner filter cake compared to when a single grade of CaCO₃ particles are loaded, indicating reduced pore damage, both external and internal. Therefore, the drilling fluid for the coreflow test included bridging particles as emanated from IPT-based calculation.

3.2. Acid Generation Rates. The rates of acid generation versus time at various concentrations of MA and EGD are presented in Figure 3. It is evident from this study that the rate of hydrolysis of EGD is significantly slower compared to MA to reach the desired concentration of acetic acid (3%) within the time limit of 3 h. Nearly 9.5% acid is produced using MA, when the initial concentration was 15% with a 0.5% catalyst, while the production of acid was limited to 4.6% when the catalyst concentration was reduced to 0.25%. These two compositions, capable of generating the optimum concentration of acid after 3 h of placement in the wellbore and attainment of wellbore temperature, were selected to substitute acetic acid in the clean-up solution. This is consistent with the recommended limit of acid in the clean-up fluid as suggested by previous authors. 

3.3. Cake Removal Efficiency of the Clean-Up Solutions. From the disc images presented in Figure 4, it is observed that the deposited filter cakes were well consolidated, and the ceramic discs appear to have nearly cleaned off the filter cakes. For quantitative evaluation, the discs were weighed before, and after tests and from the difference of weight, the clean-up efficiencies were calculated (Table 8). It is evident from this table that the acetic acid-based clean-up solution removed 92.3% of the mud cake (cumulative of internal and external). The breaker solution containing 0.5% acetic acid and

Table 7. Impact of Bridging Particles on Filtration Loss, Filtrate Quality, and Cake Thickness

| bridging particles | median size (m) | loading (gm/L) | filtration loss (mL) | filtrate quality | approx cake thickness (mm) |
|--------------------|----------------|----------------|----------------------|-----------------|--------------------------|
| very fine          | 1–4            | 90             | 18.7                 | precipitate     | 5.4                      |
| fine               | 6–15           | 90             | 16.2                 | clear           | 4.9                      |
| medium             | 16–29          | 90             | 14.5                 | clear           | 3.8                      |
| coarse             | 31–48          | 90             | 21.4                 | cloudy          | 6.2                      |
| mixed grade as per IPT as given in Table 2 | 11.7 | clear | 2.6 |

Figure 3. Acid generation rates of MA and EGD.

Figure 4. Photographs of filter cakes on ceramic disks: Top left: disc with mud cake and bottom left: disc after clean up treatment having 3% acetic acid. Top middle: Disc with mud cake and bottom middle: disc after clean up treatment having 0.25% acetic acid as catalyst. Bottom left: Discs with mud cake. Bottom left: Discs after clean up treatment having 0.5% acetic acid as the catalyst.
0.25% acetic acid as a catalyst is equally or more efficient with 93.7 and 92.6% clean-up efficiency in cleaning up the mud cake, indicating the fact that replacement of acetic acid with MA ester as a precursor can meet the objective of a low skin wellbore.

These results are consistent with earlier results of Ghosh et al., who reported that the clean-up efficiency of their investigated solution comprising 3% acetic acid and hydrolase enzyme was above 90%. Similar results are also reported by Al-Khalidi et al., through core flood studies.

3.4. Core Flood Test Results. Core flooding tests were conducted on field core plug samples to confirm the efficiency of clean-up treatments at reservoir conditions. Four core flooding tests were conducted using four similar carbonate core plugs. Two clean-up solutions were used in these tests, and the tests have been performed in duplicate. The first solution contained 15% MA with a 0.25% catalyst, used in test-1 and test-2. The second clean-up solution contained 15% of MA with a 0.5% catalyst, used in test-3 and test-4. Results of one core flood test from each set are presented in Figures 5 and 6 (i.e., core flood tests 1 and 3), showing permeability values at each stage of core treatment. The initial permeability, damage permeability, and permeabilities after damage removal treatment, along with the percentage of regained permeabilities, are presented in Table 9.

### Table 8. Composition and Cake Removal Efficiencies of Clean-Up Solutions.

| test # | disc # | MA % | acetic acid % | enzyme % | surfactant | DI water % | clean-up efficiency % |
|--------|--------|------|---------------|----------|------------|-------------|-----------------------|
| 1      | 5      | nil  | 3             | 5        | 1          | 92          | 92.3                  |
| 2      | 17     | 15   | 0.25          | 5        | 1          | 79          | 93.7                  |
| 3      | 8      | 15   | 0.5           | 5        | 1          | 79          | 92.6                  |

### Table 9. Coreflood Test Results with Regained Permeabilities

| test/core | property                                  | 1         | 2         | 3         | 4         |
|-----------|-------------------------------------------|-----------|-----------|-----------|-----------|
|           | initial permeability (mD)                  | 11.04     | 8.97      | 9.64      | 9.52      |
|           | injection permeability with mud cake (mD)  | 0.53      | 0.38      | 0.21      | 0.48      |
|           | reduction of injection permeability        | 95.2      | 95.8      | 97.8      | 94.9      |
|           | production permeability with mud cake (mD) | 4.28%     | 3.53%     | 4.10%     | 3.88%     |
|           | reduction of production permeability       | 61.2%     | 60.6%     | 57.5%     | 59.2%     |
|           | injection permeability of treated core (mD)| 9.36      | 6.24      | 8.25      | 8.61      |
|           | regained injection permeability            | 84.78%    | 69.56%    | 85.58%    | 90.44%    |
|           | production permeability of treated core (mD)| 10.87     | 8.54      | 9.92      | 9.71      |
|           | regained production permeability           | 98.46%    | 95.20%    | 102.9%    | 101.9%    |

Figure 5. Permeability results from coreflood test-1.

Figure 6. Permeability results from coreflood test-3.

It is evident that there is significant permeability damage caused due to the mud cake deposition. Injection permeability is reduced by 95% or higher, and the production permeability is reduced by nearly 60%. The severe reduction of permeability is an obvious indication of superior quality mud cake, which is also evidenced in PPTs. Post-clean-up injection permeability improved radically to 84% or higher regained permeability (except for core # 2). On the other hand, regained production permeability, which is the main objective of this study, has improved over 95% for the clean-up solution-1 and over 100% for clean-up solution-2. The higher permeability for the clean-up solution-2 can be attributed to the higher acid generation capacity of this composition. It is worth mentioning here that clean-up solution-2 with 0.5% catalyst produced 6.7% acetic acid in 6 h compared to 3.6% for solution-1 containing 0.25% catalyst. The higher concentration of acid might be responsible for more than 100% regained permeability because of acid etching of the core face and possible generation of microsized wormhole (though this cannot be confirmed with certainty).

3.5. Corrosion Rate Investigation. Based on the coreflood result, it was decided to select the clean-up solution-1 (i.e., with 0.25% catalyst) as it produced adequate in situ acid, achieved higher than 95% production permeability, and is safe for the reservoir in terms of rock dissolution. Thus, static corrosion studies were conducted on clean-up solution-1 only.
Static corrosion rates of the samples were measured in triplicate, and average corrosion rates are presented in Figure 7.

As evidenced from Figure 7, the average corrosion rate at 2 h exposure (which is the approximate pumping time) from the surface to bottom-hole temperature falls between 0.66 and 2.95 mm/year, whereas the corrosion rate after 6 h exposure at bottom-hole temperature may go up to 4.79 mm/year. The 12 h exposure (considered as the worst-case scenario in case of stuck tubular) can enhance the corrosion rate up to 6.9 mm/year. On the other hand, the corrosion rate of the recommended minimum dose of acetic acid can reach up to 9.4 mm/year at bottom-hole temperature. These results are in agreement with Dill and Keeney, who investigated the corrosion rates of several solutions of formic and acetic acids. A few recent laboratory and field investigations have also reported similar results.

Determination of corrosivity of fluid is very important, in particular when coil tubing is used for fluid pumping as it enhances tube fatigue and reduces its life cycle. According to Kalfayan, the acceptable corrosion rate of special-alloy tubulars and coiled tubing within a temperature range of 93–135 °C is 4.6 mm/year for a 24 h exposure. Comparing the measured corrosion rates of clean-up solution-1 and acetic acid, the corrosion rate of the formulated clean-up solution is less than acetic acid and meets the industry requirement. However, due to slow reaction, the solution will always remain high. As more acid is generated because of hydrolysis, the faster reaction with surrounding calcium carbonate in the filter cake would occur, producing a soluble calcium salt and ensuring a low concentration of acid at any given time. Such behavior would ensure a nearly corrosion-free environment without the need of using corrosion inhibitors. The advantage of the enzymatic clean-up fluid with MA as an acid-precursor may enable the operator to deploy coil tube without the necessity of using corrosion inhibitors.

From the above findings, it is justified to conclude that by judicious selection of bridging particle in drill-in-fluid and using enzymatic clean-up fluid with MA as acid-precursor may enable the operator (1) to minimize wellbore skin, (2) to be non-acidic when placed thus nearly corrosion-free and safe environment for downhole tools, and (3) due to slow reaction, to allow an even distribution of fluid across long horizontal sections resulting in uniform damage removal and stimulation, ensuring maximum production.

4. LIMITATIONS

The modified amylase enzyme used in this study is thermally stable for 24 h up to 270 °F. If the reservoir temperature exceeds this limit, the enzyme may have reduced activity. On the other hand, if the reservoir temperature is below 180 °F, a longer reaction time would be required. Thus, reservoir temperature and exposure time may limit the application of the recipe presented here and necessitate fresh evaluation. Moreover, for ultra-long wellbores, where the horizontal traveling time is longer, the clean-up fluid would be exposed to the reservoir temperature for a longer time prior in reaching the desired treatment zone. This would accelerate the ester-hydrolysis process and generate acid within the tubulars. Depending upon the travel time and reservoir temperature, it would necessitate a fine-tuning of the catalyst concentration and delaying the hydrolysis process.

The optimization of the bridging particle mix would vary, depending on the formation pore size distribution. The present recipe is developed based on the measured core porosity distribution. A porosity distribution study of the actual reservoir formation and recalculation of the CaCO3 grade percentages based on the IPT output is thus essential for field-scale applications.

5. CONCLUSIONS

A new drill-in fluid recipe was investigated for better clean-up, minimal damage, and lower corrosion rates. Drill-in fluid comprising several concentrations of enzyme, ester, and acetic acid was formulated based on IPT in order to minimize internal formation damage. The formulated fluid was tested successfully using ceramic disks and carbonate core plugs, resulting in extremely low injection permeability, thus ensuring low invasion of damaging material into the formation. The mud cake clean-up fluid was optimized with hydrolase and MA acid precursor, which ensured 95–102% regained permeability on field core. It was found that the solution with 0.25 wt % catalyst + 15% ester + 5% enzyme demonstrated the best clean-up efficiency within the safe corrosion limit. Core flooding results indicated that the permeability damage was minimal for the injected solution of 0.25 wt % acetic acid + 15% ester + 5% enzyme.

The corrosivity of the clean-up solution (comprising of 0.25 wt % acetic acid + 15% ester + 5% enzyme) was seen to be within the safe limit of coil tubing application; thus, the requirement of acid corrosion inhibitor can be eliminated.

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■ NOMENCLATURE
EGD, ethylene glycol diacetate
HPHT, high-pressure high-temperature
IPT, ideal packing theory
mm/yr, millimeters per year
MA, methyl acetate
mD, milidarcy
MICP, mercury injection capillary pressure
SEM, scanning electron microscopy

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