PRIMARY EVALUATION OF FILTER CAKE BREAKER IN BIODEGRADABLE SYNTHETIC-BASED DRILL-IN-FLUID

A

Thesis

by

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ORIGINALITY STATEMENT

I, Wayo Dennis Delali Kwesi hereby declare that this submission is my work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material that has been accepted for the award of any other degree or diploma at Nazarbayev University or any other educational institution, except where due acknowledgment is made in the thesis.

Any contribution made to the research by others, with whom I have worked at NU or elsewhere is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my work, except to the extent that assistance from others in the project's design and conception or style, presentation, and linguistic expression is acknowledged.

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ABSTRACT

Filter cake breakers are the means to remove filter cakes from the walls of the wellbore before completion and production. During drilling, there are layers of filter cakes formed that can't easily be penetrated; these layers prevent drilling fluids from invading the formation or an influx of the formation fluid into the wellbore; fending of blowouts. Chemical breakers are difficult to optimize, and finding a reliable way to remove filter cakes from the wellbore in a uniform manner had been a singular difficulty for researchers. Some good engineers and operators in the industry incorrectly analyze the flow of hydrocarbons into the wellbore, resulting in the designation of wells as redundant; this is due to the causes of layered filter cakes. The thesis study conducted a laboratory evaluation of several filter cake breakers using ethylene-diamine-tetra-acetic acid (EDTA), Silica dioxide (SiO2), Titanium dioxide (TiO2), and Graphene particles for better concentration optimization, and to determine how these organic acid and nanoparticles will react in a pressure, temperature regions. Also, the study formulated a biodegradable synthetic based mud drill-in-fluid (BSBMDIF) to create filter cakes using a replica of actual reservoir conditions. The methodology sought to formulate biodegradable synthetic based mud DIF which contained barite, bentonite, guar gum, caustic soda, calcium chloride, Sodium Tridecyl Ether Sulphate, graphene powder, water, and base oil, and the rheological parameters of the DIF were defined using an OFITE 900 viscometer, after which it passed the wellbore stability test. For the creation of filter cakes, HTHP filter press and Blue-M oven were utilized. Filter cakes build up in the BSBMDIF were subject to breakthrough, soaking, and injectivity tests, with the same amount of concentration measured in weights, the various filter cake breakers exhibited some level of efficiency. The organic acid, EDTA after treating filter cakes for 42 hours yielded an 80.98% efficiency, while the nanoparticles, especially Silica dioxide came close to reducing the weight of the filter cake by 69.13%. An increase in removal efficiency under this study was seen increasing the rate of return permeability, filter cakes that were treated with EDTA for 42 hours had a tremendous increase in return permeability by 74.89%, whiles graphene by contrast yielded slow permeability return by 52.97%. However, the nanoparticles under normal pressure and temperature maintained its physiochemical properties under a pressure of 100 to 500 psi and a temperature of 200°F.

Keywords: Filter Cake Thickness, Commercial Cake Breakers, Nanoparticles, Water-Based Muds, Biodegradable, Synthetic Based Muds, Drill-In-Fluids, Porosity, Nanoparticles; Silica and Graphene.

DEDICATION

God be the Glory!

A warm-hearted dedication to my single parent, Rev. Pepsy Veronica Anquandah, my late father, Vincent Kweku Wayo and to my siblings; Frederick, Bright, Kelvin, Princess and Percy who were with me through thick and thin. From this piece of my academic writing, I want to thank you all for being part of me.

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CHAPTER 1

1. INTRODUCTION

1.1 Background

For decades in the petroleum industry, the demand for hydrocarbons has exponentially increased. This has resulted many fields to be discovered and exploited in areas with an amount of high reservoir condition. Technology over time has made drilling in these harsh conditions very simple to do due to the progressive drilling developments. Such technologies can be considered among others, the engineering of drilling muds or fluids has aided the simplicity of drilling operations.

These muds are designed from various suitable chemicals, solids and liquids which a pumped from the mud pit into the wellbore to aid smooth drilling operations. The primary aim of these carefully engineered muds or drill in fluids are to carry cuttings from the wellbore to the surface, cool down the drilling bit, stabilize the well by controlling the hydrostatic pressure as against the formation pressure and as well keep the drilling string lubricated. [1]. During this period of circulating the drilling mud in the wellbore a cake is formed in the wellbore that could be as a result of an aqueous or non-aqueous based drilling fluids during drilling operations.

These cakes protect and stabilizes the formation from fluid invasion which allows an enhancement of mud circulation through the wellbore. Correctly engineering the drilling mud and choosing the additives to be used produces a filter cake with good characteristics. These cakes have the inclination of reducing the drilling complications during operations as it can resist high differential overbalance pressures in the wellbore.

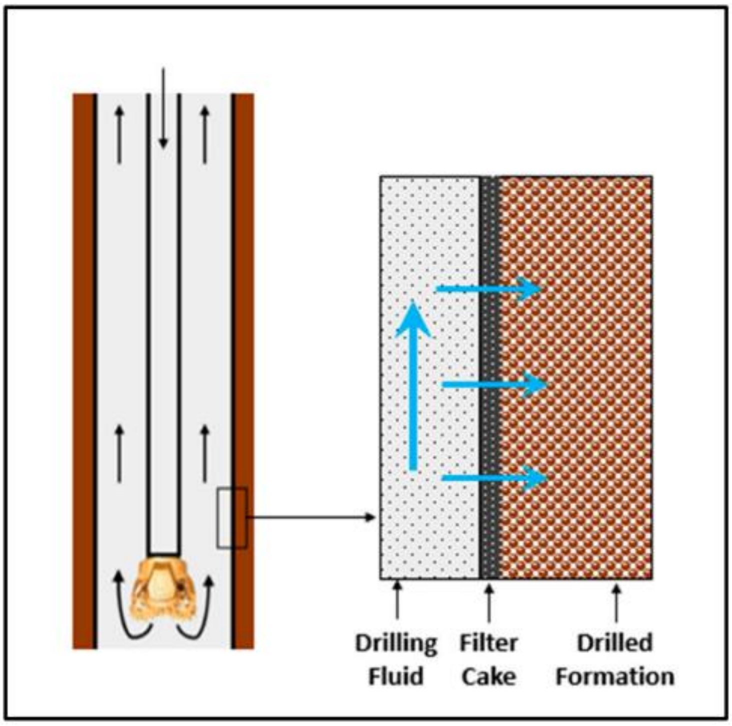


Figure 1. Thin layer filter cake formed on walls of wellbore [48]

Cakes can be regarded as a tool to averting formation damage and increase permeability return in the wellbore [2]. Whiles intending to understudy the effective use of filter cake breakers to removing the non-aqueous based mud drill-in-fluid, the research paper seeks to consider the importance of all wells that are designed and considered to be completed in open hole or pre-slotted liner as sand control mechanisms. In estimation, very limited literature papers had shown the efficacy of filter cake breaker in removing the biodegradable synthetic based mud drill-in-fluid filter cake and vividly explained the mechanism of filter cake breaker. Therefore, the reported successful applications of filter cake breakers were easily available for water-based mud drill-in-fluid compared to synthetic based mud drill-in-fluid. Hence, this study had a significant note in validating the production of several commercial filter cake breakers in removing synthetic based mud drill-in-fluid filter cake.

The synthetic based mud drill-in-fluids are substantially used to move the cuttings from subsurface through the annulus to the surface of the well, these drill-in-fluid has the capacity to reduce the friction between the wellbore and the drilling pipe as these processes cools down the drilling bit, it maintains the stability of the well preventing the intrusion of formation fluids into the wellbore as it creates a thin layered filter cake. The other section of cakes under study is described as a starch that has the tendency to increase viscosity stimulate fluid loss control.

The production of hydrocarbons in the wellbore reduces due to the layers of filter cakes formed in the wellbore this reduces flow capacity. To increase the said flow, filter cakes are removed by employing the usage of mineral acids and oxidizing agents.

Research has proven that these acidic and oxidizing agents are not suitable for unconventional wells but only for removing previous filter cakes in the wellbore and hence shoot up the permeability of the hydrocarbons in the wellbore before completing deep cake removal [3].

Moreover, there has been an improved removal using chelating agents and nanoparticles to removing filter cakes from unconventional wells and increasing flow capacity in the wellbore [4].

1.2 Problem Statement

Most petroleum industrial players in the years past have one way or the other abandoned wells over the assertion that the wells are no longer productive as this could be associated with formation damage due to drill in fluids forming skin damage during mud circulation in the wellbore.

A resilient way of formulating biodegradable Synthetic based mud to resolve the problems associated with borehole cleaning and wellbore stabilization was a concern to the study.

The confronting challenge of the thesis is how to create an efficient way of formulating an optimized concentration of filter cake breakers using nanoparticles such as silica dioxide, titanium dioxide, and graphene. An environmentally friendly organic acid, EDTA, was considered, all under high temperature zones for the effective removal of filter cakes.

The final problem considered in this study was to define return permeability by running an observatory analysis to finding an effective degradation process of breaker solution in temperature and pressure zones.

1.3 Thesis Objectives

The main purpose of the thesis is to determine the optimal concentration of filter cake breakers, such as SiO2, TiO2, Graphene, and EDTA, for eliminating biodegradable synthetic mud drill-in-fluid filter cakes under temperature and pressure conditions. The project also intends to create a more resilient biodegradable synthetic mud with guar gum as one of its base ingredients, as well as assess the performance of the breakers in removing filter cakes from the ceramic disc and define return permeability.

1.4 Significant of Study

The significant challenge of the petroleum industry is the threat of insufficient hydrocarbon flow from the formation to the wellbore. As a result, wells are readily abandoned, and the cost of drilling, completing, and producing new wells continues to rise. The difficulties connected with filter cake build-up and removal on the wellbore's surface are what makes this research study so interesting. The thesis looks at different ways to optimize filter cake removal in the laboratory, by using the same concentration of chemical components measured by weights (grams). Fluid completion engineers, and petroleum industry players in Kazakhstan would have an additional alternative rationale to applying these findings in the fields or be applied as a literature for upcoming students in the school of mining and geosciences.

1.5 Thesis Organization

The thesis is organized into four chapters, with the first presenting and reviewing the literature on filter cake formulation and filter cake breakers. The problems and goals of the study are also discussed in this chapter. In the second portion of the structure, you'll find materials, equipment, and methodologies for performing filter cake build-up, breakthrough, soaking, and injectivity experiments for filter cake breaker evaluation. The study's third chapter, on the other hand, summarizes the results of the test conducted in chapter two, while chapter four discusses the conclusion and makes recommendations for further research.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Drill-in-Fluids

The usefulness of synthetic based mud drill in fluids has been widely recognized by drilling engineers and industry players over centuries. Most often than not, finding the fluid choice during drilling operations depends solely on formation structure and intended drilling depth. In considering deep-water regions, the prime fluid must be considered due to the advantage to attain high penetration rate and stability of wellbore.

There are several chemical substitutes that can be used in place of oil muds when considering synthetic drilling mud formulation. Fluid type under consideration may not only be driven by cost but the toxic nature of the fluid under question is critical in selection. Diesels are considered toxic due to the presence of aromatic molecular structures. Diesel substitution in fluid design is to reduce the aromatic content in it making it environmentally friendly and less toxic. If this toxic reduction is well considered and accepted by regulatory authorities, then it can be however used for the fluid design in the laboratories and for drilling operations in the industry. The molecular structure and chemistry are made considerate for biodegradation for safe use to the environment. These structures that contains oxygens in the fluid material design degrades much faster.

Research has proven that the defiance of the synthetic based muds has possible circulation loss into formation as this happens when the muds or drill in fluids has been invariable for a period. Drill in fluid viscosities is increased in cold temperate regions which turns to affect surge pressure and equivalent circulating densities. The associated cost and time relating to synthetic based muds are as a result of the drilling margins in narrow form operated in deep-water regions, this increases unbearable rheology which at the end breeds terrible losses of drilling mud. To simply eradicate this problem, the researcher paid much attention on the fluid rheology. Proper fluid rheological formation would control the equivalent circulating densities; the lighter the fluid yields the lower the equivalent circulating density. Whiles the concentration is on fluid rheology in certain wells, the fluid should be a mastery in removing the cuttings from the wellbore to the surface and the suspension of barites.

Figure 2. Problems associated with barite sag; borehole instability, poor hole cleaning [5].

However, the most difficult aspect of designing fluid rheology is the intention to carefully stabilize equivalent circulating densities, suspension of barites in the wellbore and hole cleaning. Synthetic based mud research and design has become necessary because of its promising feature to solving deep-water drilling operations [5]

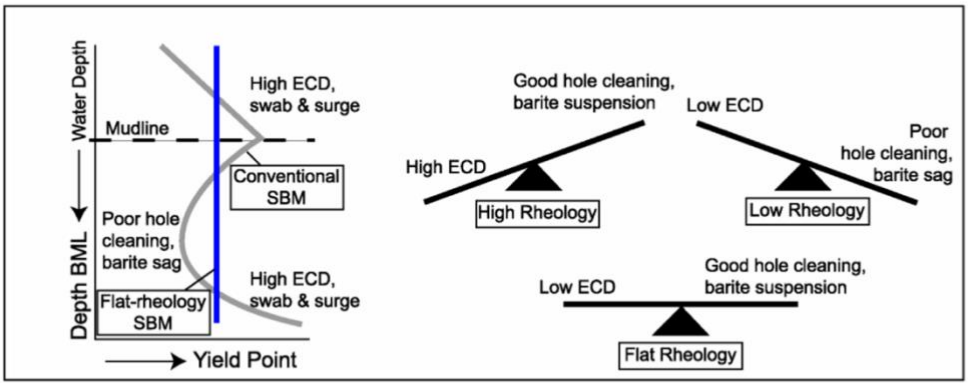


Figure 3. Left figure indicates an independent mud rheology suitable for deep water reservoir conditions. On the right also indicates a stable mud rheology [5].

Laboratories has the limitations of finding the direct impact of these fluid design below subsea though they study the conditions at the bottom of the sea it is only for assessment. [6]. Contrary to water-based mud drill in fluids, synthetic based mud drill fluids have higher rate of penetration and wellbore stability especially when calcium carbonate is one of the ingredients in the preparation of the drill in fluid. Some limitations of synthetic based mud drill in fluid over time of its successful application were existing issues of emulsion blocking and wettability. Under circumstances, the water-based mud drill in fluid was preferred as further research was conducted seeking for additional additives to making the synthetic based mud drill in fluid suitable.

The synthetic based mud drill in fluid has its’ emulsion inverted as water in the internal phase while based liquid or oil was in the external phase. Moreover, the synthetic based mud drill in fluid had it wetting condition reversed from oil-wet to water-wet and a decline of its acidity to neutral. This is considered when the synthetic based mud drill in fluid filter cake is in acidic nature due to its’ chemical treatment.

However, the addition of proton molecule changes the stability of synthetic based mud drill in fluid which leads to the conversion of the strong emulsion to weak in the ionic region. To this essence the synthetic based mud drill in fluid has functioned as an invert emulsifier making drilling operations suitable because it has the mud behaving in double ways. Also, filter cake removal from this synthetic based mud drill in fluids are made easier during completion periods. During the formulation of filter cake breakers to complete wellbore has an amount of added non-emulsifier solution. As this solution is necessary it makes the formation water-wet aiding the process of removing oil from the formation; if formation is water-wet, it supports particles to be cleansed and be dissolved more easily.

2.2 Compatibility of Fluids

To have a more satiable efficiency of hydrocarbon flow from the open hole, fluid compatibility is very necessary to prevent undesirable chemical reactions with other fluid chemical compositions so it doesn’t hamper the essence of filter cake breaker formations when pumped into the wellbore.

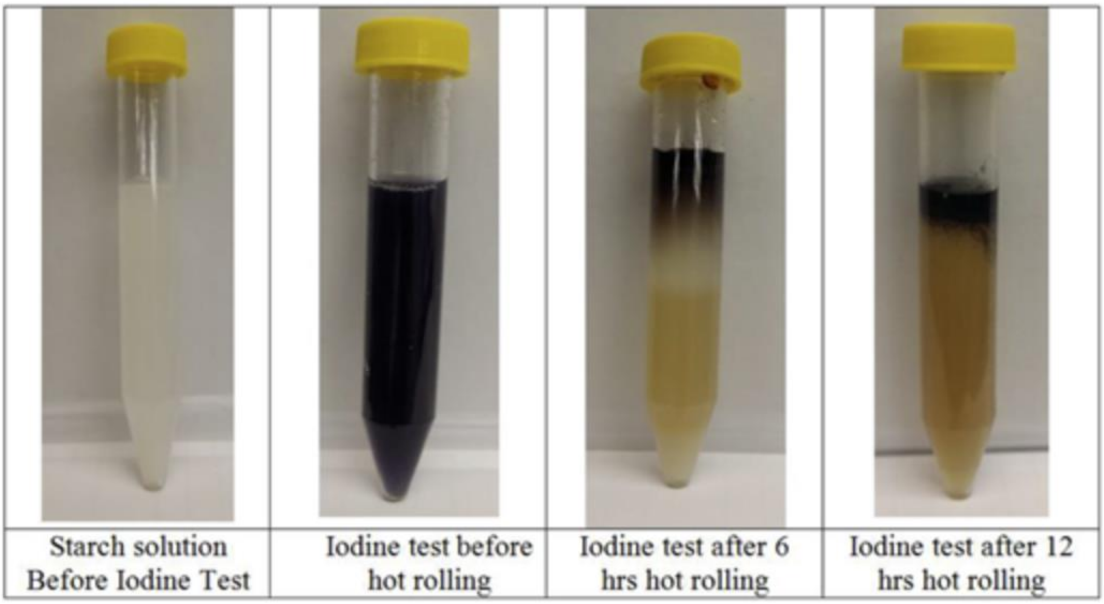
Not designing the chemical composition of fluid skillfully can lead to fluid incompatibilities that could result in formation damage hindering well completion performance.

Laboratory research emulated a harsh reservoir condition using a high pressure and high temperature carrier cell for the testing of fluid compatibility between chemicals. Diverse test was conducted at different low and high temperatures. Diethylene-triamine-penta-acetic acid, a chelating base was added to solid free base potassium formate-based brine in an equal proportion but failed to break. [7]

This is because the chelating base failed to remove the calcium carbonate particles, an ingredient in the synthetic based mud drill in fluid.

The research conducted demonstrated the ineffectiveness of chelating base in breaking cakes because the bridging agent was made of a coated biopolymer. Same laboratory test was conducted for filter cake breakers and brine at set ratios.

The filter cake breaker was formulated with a chelating base in calcium chloride brine which at the end of the research demonstrated a good compatibility with completion fluid. Besides that, compatibility of enzyme added into filter cake breaker formulation had been investigated. Moreover, a laboratory analysis was carried out that resulted in chelating agent such as DTPA, ethylene-diamine-tetra-acetic (EDTA) acid with pH 8 and glutamic-acid-tetrasodium-acid (GLDA) with pH 7 and 12 showed incompatibility with amylase enzyme.[7]



Starch solution Before Iodine Test

Iodine test before hot rolling

Iodine test after 6 hrs hot rolling

Iodine test after 12 hrs hot rolling

Figure 4, Assessment of EDTA breaker to starch removal [49].

2.3 Nanoparticles: Silica-particles

Most petroleum industrial players in the years past have one way or the other abandoned wells over the assertion that the wells are no longer productive as this can be associated to formation damage due to drill in fluids forming skin damage during mud circulation in the wellbore.

An effective ultra-thin layered wellbore damage is removed by a steady dispersion of nanoparticles that has a sized 4-20nm silica as it constituent. This is used to remove skin damage that are linked with paraffins and polymer strands in the wellbore to aid the production of hydrocarbons. The positioning of the molecular structure of these particles aid in the rapid lifting of the thin layered skin damage from the surface of the wellbore. This helps stimulate the well for productivity.

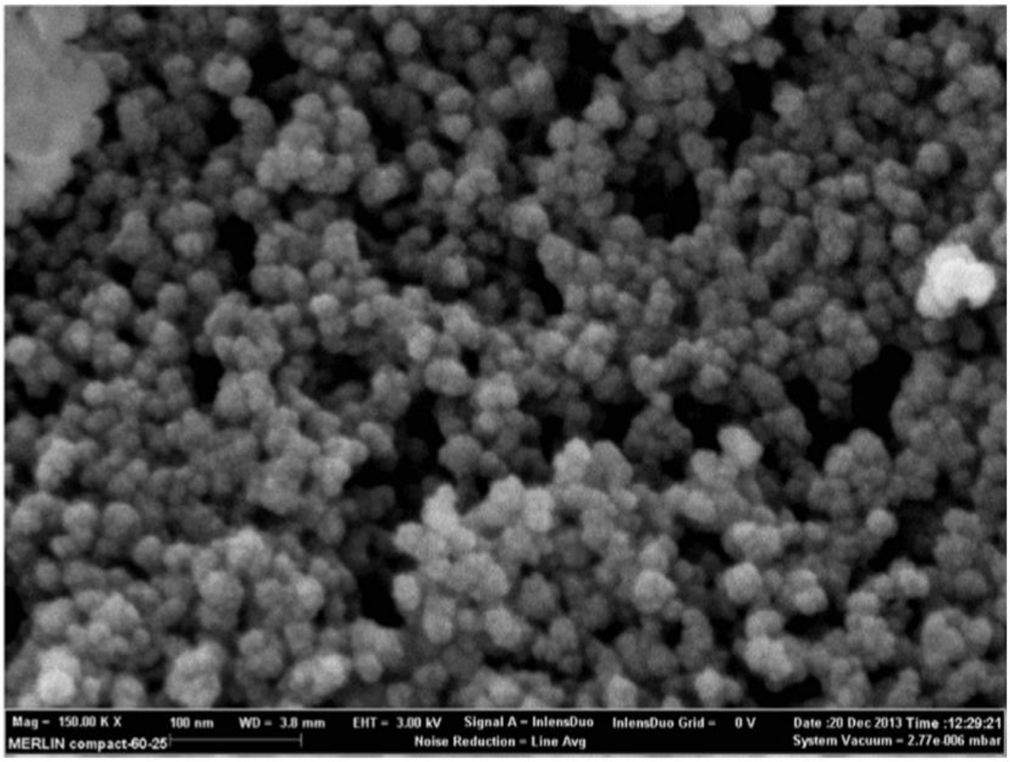


Figure 5. SEM Dispersion of silica particles

A water-based dispersion of these particles as shown in fig 4. is in connection with a conventional means can be used to efficaciously remove the damage from the wellbore instead of melting skin damage that could eventually be displaced into the formation [8]

These formation damages are the natural occurrences of paraffin blocks during drilling operations and some well interventions during the life of the well cycle. To this end, this could portray a none viable well for a declined economic gain and subsequently be abandoned. [8].

Polymer strands and paraffin blocks that causes skin damage has always posed a challenge to the industry players. During the well’s initial periods of production, the hydrocarbons are lighter at it beginning. But as time passes, the well begins to produce a thicker or viscous fluid where paraffin blocks are accompanied; pressures and temperatures at this phase of the well are reduced in the bottom hole.

The researcher also sought to use solvents like hot oil treatment (xylene) to melt the paraffin blocks in the wellbore which must be conducted regularly; solvent at this moment naturally disintegrate the paraffins near the wellbore to and further moves it into the formation. Whiles these treatment goes on in the wellbore, an amount of paraffins are successfully produced but some remains in the formation undissolved which will require a regular well stimulation for hydrocarbon recovery at a more justifiable economical means [8].

An additional source of skin damaged that is caused by polymer invasion has as well posed production threats to the well. During hydraulic fracturing, the complexity of these process turns to damage the formation by way of polymers occupying the rock matrix. Polymer strands that are formulated in drill in fluids has its structures broken by an enzyme, oxidizer or a conventional acid to aid production; this operation is guided by hydraulic fracturing by pumping half percent of fluid downhole. As a result, most of these polymers are left trapped in the formation or rock matrix. Left over polymer fluids consequently affect the overall performance of the well.

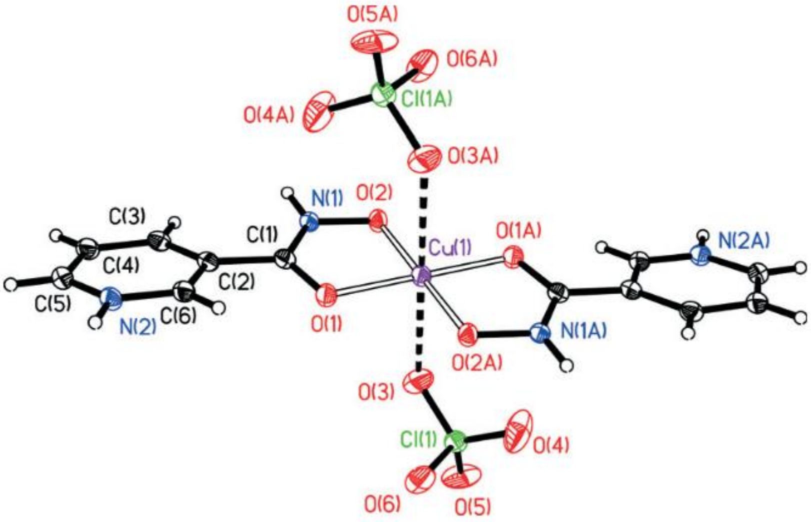


Figure 6. Molecular Structure of Polymer Strands [50]

To resolve the formation damage, a workover process is required to aid pump suitable filter cake breakers downhole; this process is seen more typical a resolution other than dissolution of paraffins that further runs into the reservoir. Though these treatments have yielded results mitigating the formation damage but some have disappointing results. The very goal is to reduce or eliminate the damage from the face of the fracture as to allow the well to produce efficiently and not to break of the flow of hydrocarbon production which may intend require further future interventions. It has been noticed in laboratory testing that the newly developed fluid system has the ability of stabilizing water-based dispersion of silica nanoparticles with a diameter sized of 4-20nm to be potent in removing the skin damage relating to polymer and paraffins. This employed fluid system works adversely to the current working methods that merely dissolves and displace formation damage. Brownian motion is utilized in allowing sized nanometer particles behave as detergents and tendency of disconnecting pressures on the top of the rocks.

The water-based nanoparticles dispersion that are tried with some traditional dissolution methods in test fields has proven effective in removing skin damage because it has the tendency of savaging problems associated with two-phase. The oxidizing content solvent with nanofluids are able to remove bulk skin damage from the rock which after dissolving are able to be transported out of the well. This has demonstrated it cost effectiveness because wells under this breaker solvent composition will require less frequent treatments [8].

In the year 2003, Wasan and Nikolov [9], stated the first description of how ultra-smaller particles work were demonstrated by them in the Journal Nature. These nanoparticles in structural arrays disperses in a discontinues paraffin and polymer phase. The fluid particles that are in three phase regions tend to present itself into a wedge-like structure that launches in between a discontinuous phase and the substrate. Particles in bulk fluids has a continuous propensity to shoot particles into confined regions forward and in return disjoints the binding pressure forces. Form this description is an obvious definition of Brownian motion and electrostatic particle repulsion.

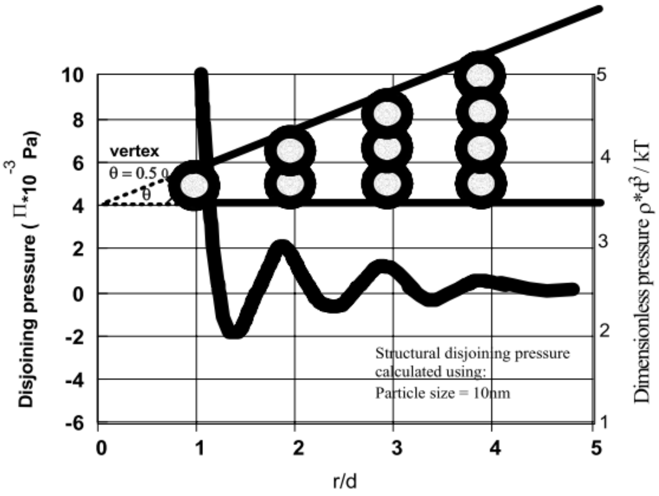


Figure 7. Shows an extent of detaching pressure [51].

The energy in attacking single particles is weaker than a volume of particles and this pressure build up can be moved to an extent of 50,000pa. Not limited to, the strength of these force can be lessened by particle charge density; the higher the charge density, the larger the electrostatic repulsion between the particles. Also, the temperature, salinity of the fluid carrier, particle size and surface features act on the mechanism extend [8], and again they examined the spread of the nanoparticle fluids on top of solid surfaces [10], the energy of disjoining pressure is directly connected to the tendency of nanofluid to spread along the membrane. It is necessary to have the same charge of the membrane and the suspended particle.

Nanofluids flow on the surface of the rocks as monolayers when there is a constant repulsion of two liked charged surfaces; this was demonstrated with contact angle experiments. Silica nanoparticles has proven a lower contact angle than that of water on a liked charged surface glass plate. Nanofluids has however been demonstrated to have acted as a wetting agent where paraffins and polymers are successfully removed leaving water-wet [8].

The tested laboratory nanofluid particles were used to compare the standard industrial polymer-based fluid loss additive for its effectiveness. The experimented rheological properties yielded positive results without any excessive difference from the standard polymer-based additive an is mainly used for fluid loss control.

A higher shear viscosity is better gained with nanoparticles as bore-plus has a direct response to several shear rates. The very aim of the project was to investigate the reactions of nanoparticles as fluid loss additive. Samples were subjected to a temperature of 70 F and a constant pressure of 100psi in a standard API filter press and measured the quantity of fluid loss through a ceramic disc and filter paper. Further fluid loss additive comparisons were made with nanoparticles and the sampled particles.

2.4 Nanoparticles: Graphene-particles

In recent years, research on the application of nanomaterials in biology, medicine, electrical engineering and other fields has developed rapidly, furnishing latest ideas for the development success of the oil and gas industry.

The comparative increased cost of nanoparticles presents a major challenge for oil and gas applications. However, scientists and oil companies around the world are actively studying the use of nanomaterials in the oil industry.

The most frequently studied nanomaterials are carbon nanotubes, carbon nanofibers, nano oxides, and nano-clays [1] More and more attention are paid to the use of graphene and its derivatives in the oil and gas industry as a special nanomaterial. Compared to those widely applied in other fields (such as biodegradation, biomedicine, electronic energy storage and conversion devices, electronics, photonics, high strength composite materials, etc.) [11].

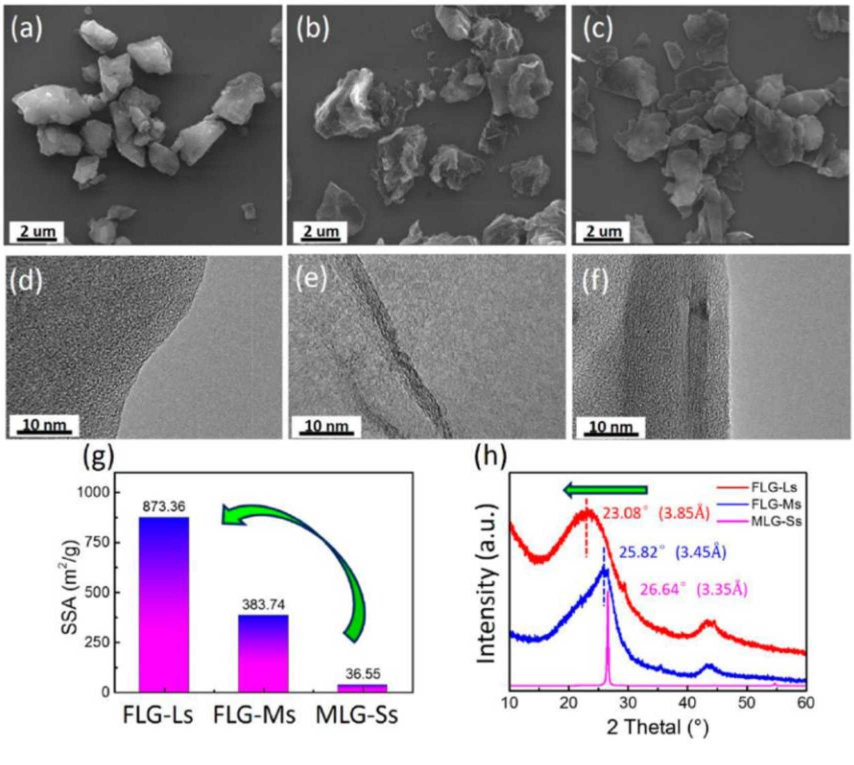


Figure 8. SEM characteristics of Graphene Nanoparticles [52].

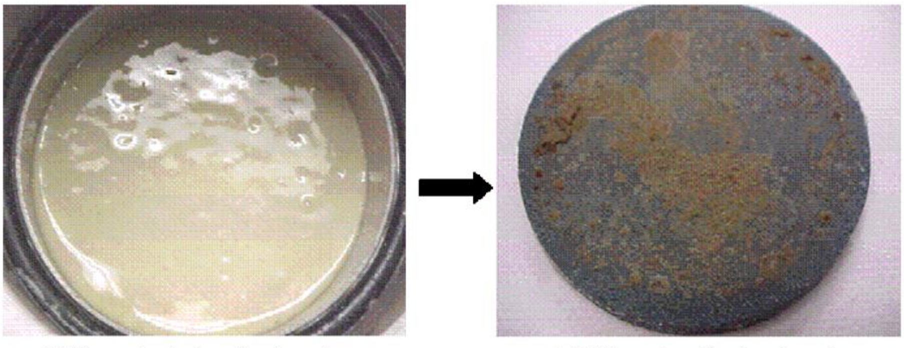
The impact of graphene and its derivatives on oil exploration and development is clear. Many scientists and engineers believe that this is most likely applicable to the oil and gas industry. In theory, graphene should be large and large, but each carbon atom is sp2-hybridized and has an independent bond at the edge.

However, since graphene must be stable in its natural environment, the pendant bonds at the edges of the nanoscale graphene layer are occupied by other chemical bonds, making it a three-dimensional graphene material, which in practice always consists of nanoscale graphene. layer. This article describes the applications of graphene and its derivatives in petroleum engineering and provides guidance for the development of the petroleum industry [11]

2.5 Chemical Filter Cake Breaker: Acid or Oxidizer Based

Traditional acids or oxidizing base are the most acceptable means of removing filter cakes from the wellbore, even though there are some limitations to it usage.

Acid in its usage is corrosive and using it to remove filter cakes from the wellbore had complications with the equipment or tools used in the field when they come into contact. This poses environmental health hazard to the individuals handling the acidic filter cake breaker on the surface and as well as the formation. Due to the rapid reaction of the traditional acid for treatment, there was an observed results of an incomplete filter cake removal in designated location. For this reason, there was a reduction of permeability of the hydrocarbon through the filter cakes to the wellbore due to the incomplete filter cake removal reactions, however the improper usage of these traditional acids used in the



a) Filter cake before treatment

b) Filter cake after treatment

Figure 9. Effects of hydrochloric acid in CalCl2 brine [18]

wellbore to increase the permeability profile of resulted in to cost of re-stimulating the wells to restore production.

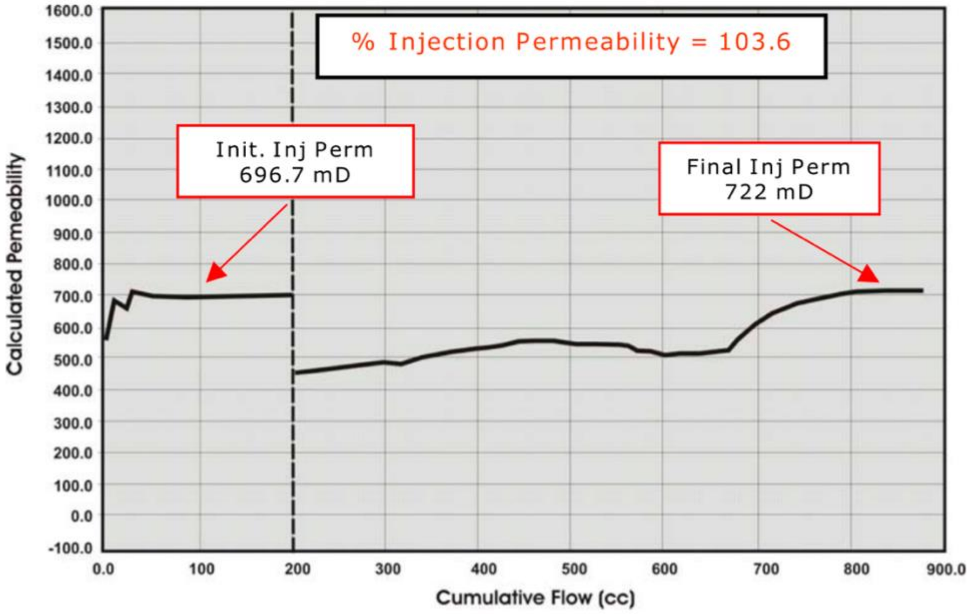


Figure 10. Observing permeability Return

Filter cakes that contained dissolved solids and biopolymers had an active acidic breaker striking the strands of polymers and other substances that were bare to the acid or oxidizing base which caused a serious damage to the formation. This is because the main constituents of the polymer strands in the filter cakes had not been successfully dissolved or broken and that posed a challenge to the formation as the cross links of the polymer strands were incomplete. The chemical composition of the traditional acidic structure was made necessary because it had the tendency of removing all the gaps and mass of the filter cakes components.

For a more efficient filter cake removal, the traditional acidic treatment needs a further touch and review as it is necessary to fully break the components of the cake to allow sufficient flow of the hydrocarbons from the formation into the wellbore.

2.6 Chemical Filter Cake Breaker: Enzyme-Based

The filter cake breakers formulated from enzymes were made to find and crack certain linkages that were found in various polymers. The formation was under siege as the cake breakers made of enzymes couldn't attack polymers with sole enzymes. Filter cakes under the attack of the enzyme-based filter cake breaker was able to remove the thin layered cake from the wellbore through a catalytic means.

During this process of removal, the enzyme base produced soluble sugar pieces on thin layer that were not harmful to the formation, on the contrary this enzyme-based filter cake removal has its limitation on degrading polymers under low temperate wells.

An upgraded enzyme-based filter cake that was capable to break not only starch but also xanthan gum and schleroglucan was designed to allow an effective filter cake removal [12]. Although enzyme-based filter cake breaker was designed for water-based mud drill in fluids, a laboratory study had been conducted to test the effect of calcium-based brine system which was typically used in synthetic based mud drill in fluids towards the activity of the specific enzyme. Based on the result, Enzyme X with 1.15 % by weight reflected increase in turbidity when mixed with 10 % calcium chloride and 5 % calcium bromide. This was due to enzyme salting out effect of having lower calcium bromide concentration compared to calcium chloride. When tested with concentration of 30 %, enzyme salting out had occur, but the turbidity reduced and the solution became transparent again. This event was caused by hydrophobic reaction between the denatured enzyme and the salt ion. While the solution became transparent again, the enzyme was totally unreactive and became completely ineffective. This study was remarkable as the outcome explained why enzyme-based filter cake breaker was not suitable for SBMDIF filter cake removal [12].

The degradation activity of Enzyme X to dissolve necessary solids in the filter cake which marked calcium chloride-based brine as having the worst capability to remove the filter cake.

Table 2. Degrading various starch with commercial enzyme (**) and pure solution (*)

Polymer	**Enzyme A (U*/mg)**	**Enzyme B** (U*/mg)**	**Enzyme C** (U*/mg)**
Maize starch	0.30	0.030	0.020
Starch I (low crosslinking degree)	0.28	0.003	0.005
Starch II (high crosslinking degree)	0.048	0.001	0.001
Scleroglucan	0.0002	0.130	0.095
Xanthan Gum	0.0002	0.060	0.050

Table 2. Examining the permeability % of scleroglucan-Starch with enzymes

	Enzyme A	**Enzyme B**	**Enzyme C**
Initial permeability [ki] (mD)	62	66	64
Final Permeability after enzyme treatment [kfe] (mD) **(kfe/ki %)**	52 **(83%)**	53 **(80%)**	55 **(86%)**
Final Permeability after formic acid (5%) treatment [kf] (mD) **(kf/ki %)**	61 **(98%)**	63 **(95%)**	64 **99%)**

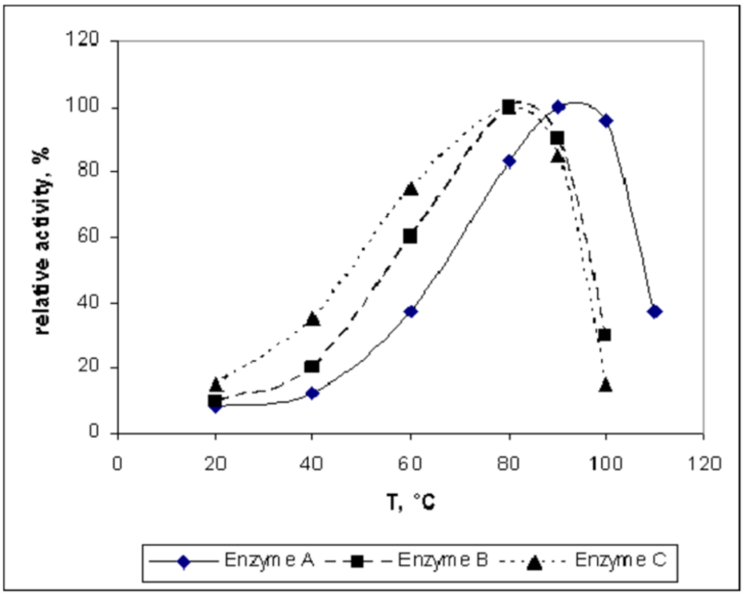


Figure 11. Influence of temperature on enzymes [12].

Attention has been drawn on the successful draining of hydrocarbons from the formation to the wellbore from different angular sections of the well to satisfy free fluid flow. New technology for this breaker enhancement has features to drill horizontal wells.

This breaker formulation has an environmental restriction from the local authorities restricting the use of toxic but degradable substance. This reason is justifiable because it has the ability to access wells horizontally [6]. There has been several chemical compositions and polymers that had been used to formulate synthetic based mud drill in fluids to target some requirements of mud design [13]. These systems depend solely on polymer adsorption within the rock pores in the reservoir.

Moreover, the drilling mud that contacts high yielding zone is capable of reducing well productivity by mud invasion due to deposits of polymers as a mud cake on the wellbore wall that may stop the flow. There is a starch component in no artificial polymers that are widely considered for drilling operations, well stimulations and other well applications as these behave as additives by furnishing the wellbore with filtration loss control, reduction of friction and viscosification.

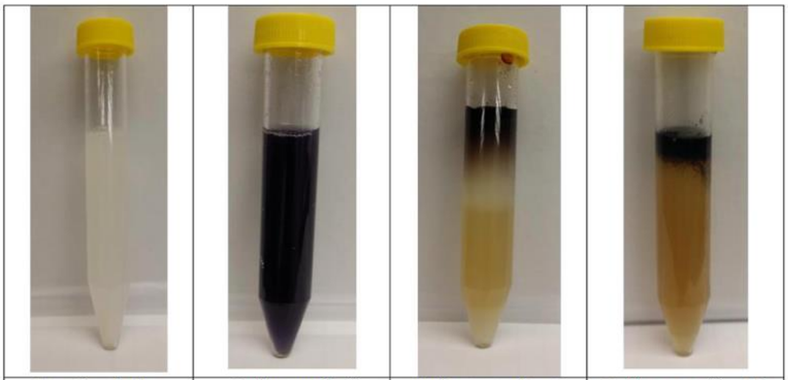
Polymers with ionic structures when added to water flooding gives rise to hydrocarbons flow pace by increasing it volume in the reservoir. This is because oil is enhanced through the rock pores as it is displayed on the surface and the tendency of reducing permeability of water. By these processes polymers forms thin layers of filter cakes blocking the pores of the reservoir rock not allowing the free flow of fluid from the reservoir to the wellbore [11].

2.7 Chemical Filter Cake Breaker: Chelating Based

Chelating agents such as EDTA, hydroxy-ethyl-diamine-triacetic-acid (HEDTA), DTPA and MTA had been suggested to be a newly designed biodegradable filter cake breakers that could enhance efficiency in filter cake removal [15]. This chelate-based fluid had been proven to effectively dissolved the bridging agent in the filter cake which was calcium carbonate causing the removal of the filter cake to be successful.

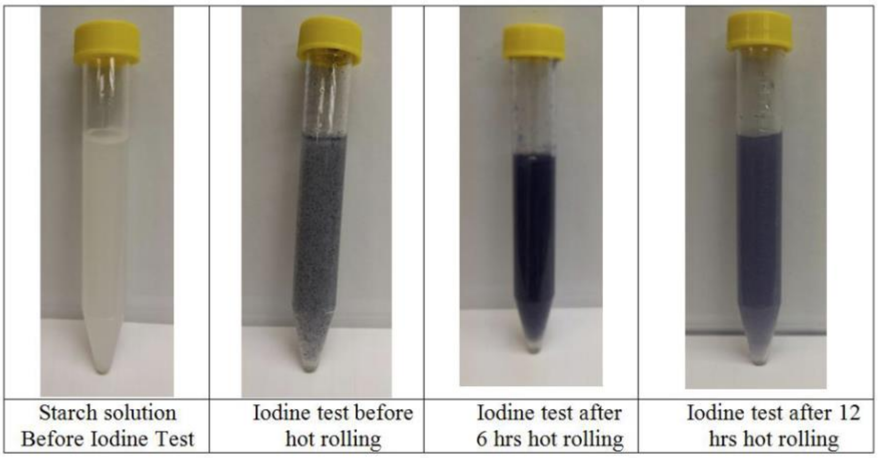
Dissolution of calcium carbonate by chelating-based filter cake breaker was dependent on the solution pH. Besides that, the ability of the chelating agents to provide low corrosion potential made chelating agent as a great alternative for live mineral acids. This provided less aquatic toxicity, more human and environment friendly and readily biodegradable filter cake breaker. The chelating agents were better than the available products which had high toxicity and low solubility.

Moreover, chelating agent- based filter cake breaker was a versatile chemical to be used in various types of formations where emulsion formation could be hindered [16]. Combination of any of the followings such as formatted-based brines, live mineral acids, hydrochloric acids, organic acids and chelating agents were conventional chemicals used to remove Oil based mud drill in fluid filter cake.



Starch solution Before Iodine Test	Iodine test before hot rolling	Iodine test after 6 hrs hot rolling	Iodine test after 12 hrs hot rolling

Figure 12. Evaluation 20 wt% at pH 12 to dissolve starch at a temperature of 200°F, [49]



Starch solution Before Iodine Test

Iodine test before hot rolling

Iodine test after 6 hrs hot rolling

Iodine test after 12 hrs hot rolling

Figure 13. Evaluation 20 wt% at pH 7 to dissolve starch at a temperature of 200°F, [49]

On the contrary, combination of chelating agents such as GLDA and HEDTA was a great recipe to remove water-based mud drill in fluid filter cake [17].

Chelating-based filter cake breaker had been successfully applied to remove reversible reservoir drill in fluid. This breakthrough technology allowed the water-in-oil emulsion to be converted into oil-in-water emulsion to provide wellbore stability during drilling operation [17]. When required, the oil-in-water emulsion could be easily converted back into water-in-oil emulsion by using chemical switch such as acid or base that was favorable for completion stage. Soaking test was performed with chelating-based filter cake breaker with pH ranging from 5 to 12.

The flowback test conducted also showed a positive outcome where 82.7 % return was obtained when soaked into the filter cake breaker for 72 hours.

2.8 Internal and External Filter Cake Removal

Recovery of hydrocarbons subsurface has been a crucial means to meeting the worlds petroleum demand. In the wellbore, to eliminate the skin impairment that had been caused by filter cakes from drill in fluids is a most happy ending means to do, as this restores the well allowing the easy flow of the hydrocarbons from the formation to the wellbore.

A cost-effective but durable filter cake breaker is needed to help clean various open-hole completion operations and some other applications to build up a better flow regime. The appropriate means to this cleanup is the surfactant technology. This, when added accurately with the traditional acid allows an invert emulsion cleaning which is referred to as a one-step cleanup. The invert emulsifier filter cakes are found in surfactant solution, and it is made soluble in the traditional acids allowing it to decay.

Laboratory experiment on Berea sandstone and several formulated drill-in-fluids indicated that the permeability profile of this core in question was being injected with surfactant and traditional acids for the elimination of filter cakes, this proofed that, the surfactant technology on display had noticed a water-wet condition and particles were removed by acid. This is the most appreciable means in removing filter cakes to enhancing hydrocarbon recovery [18].

Also, it is much easier to make out filter cakes removal externally than observing it internally. By observation the external cake removal after soaking the core was seen to have maintained a good permeability profile. This test indicates that the filter cake breaker for this experiment is a good one.

In comparison, to determine the existence of filter cake internally is so hard to see. Internal filter cakes were related to spurt loss as the drill in fluids was seen entering the formation or into the core sample, in observation it was realized that the process had formed a good filter cake. For this reason, the internal filter cake had reduced the permeability profile and however distorting the balance of the formation or the core sample. A permeability profile was tested in the laboratory to determine the extent at which the internal filter cake or the internal formation damage had occurred, this was however done after the removal of the external filter cake, another permeability check on the internal formation damage was done again. In analysis, it was confirmed that the rate of permeability reduction profile indicated that there was the presence of internal filter cake formation. To eliminate the internal formation damage or internal filter cake, then we needed to introduce injection of acid into the formation to increase the permeability profile.

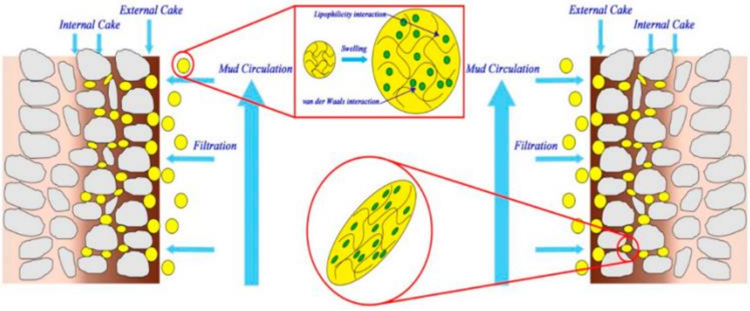


Figure 14. Schematic view of internal and external filter cake, [53].

2.9 Effects of Concentration of Filter Cake Breaker

Filter cakes breakers understudy is considered to be Silica dioxide (SiO_2) and Ethylenediamine tetra acetic acid (EDTA). These are further discussed to understand the relevance of the research conducted.

Silica has an effective ultra-thin layered wellbore damage that is removed by a steady dispersion of nanoparticles sized 4-20nm.

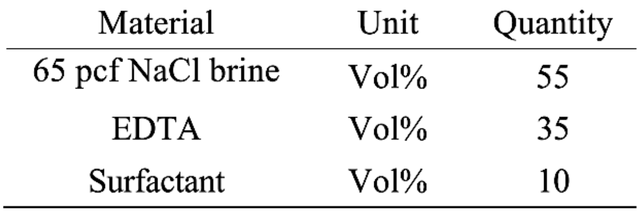
This is used to remove skin damage that are linked with paraffins and polymer strands in the wellbore to aid the production of hydrocarbons. The positioning of the molecular structure of these particles aid in the rapid lifting of the thin layered skin damage from the surface of the wellbore. This helps stimulate the well for productivity.

A water-based dispersion of these particles in connection with a conventional means can be used to efficaciously remove the damage from the wellbore instead of melting skin damage that could eventually be displaced into the formation [8]. A good concentration of nanoparticles in the drill-in-fluid design is to create a none erodible and impermeable membrane that would be created around the wellbore to check spurt loss, drill in fluid loss, clay swelling during circulations in the wellbore. Nanotechnology can get rid of the use of some additives, rheological modifiers and shale inhibitors when conducting a clean-up before well completion [19].

Research has also proven that, a better way of composing good concentration of Ethylenediamine tetra acetic acid (EDTA) has been observed and evaluated, and the reactions of this chelating agent effectively remove filter cakes in synthetic based muds. According to [4] EDTA has a higher tendency of removing or breaking the formulated polymer strands in filter cakes with a uniform slow reaction which reduces corrosion and alleviates emulsions, [20]. This chelating agent contains metal ions that uses it capacity to control or block reactive sites from entering the unwanted reactions [20]–[22]. The control is done by introducing a more stable structured ring which occupies all the active focal sites [21], this is further explained as molecules carrying a negative charge is able to bond amino and carboxyl groups with metal ions (M+n) [21]. EDTA among other chelating agents are widely used in the industry as it carries a weak organic acid compound [20].

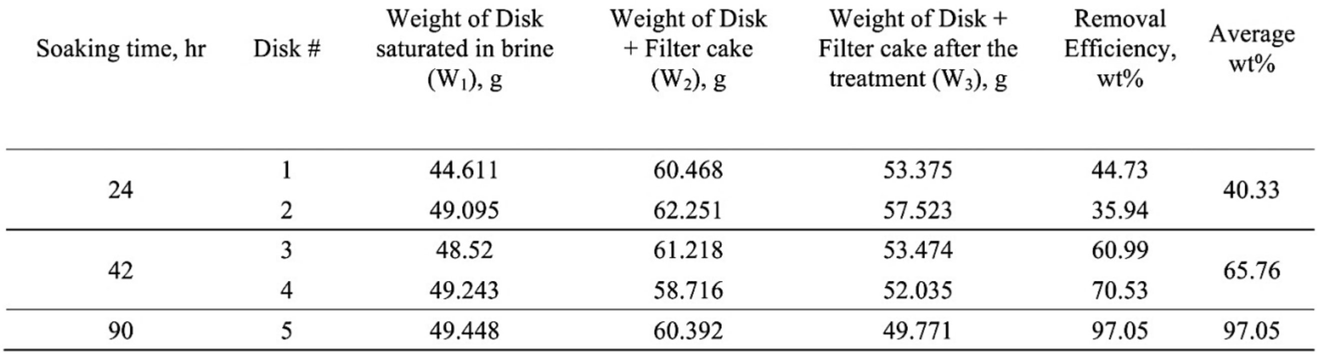
[16] experimentally measured the effectiveness of EDTA in complementing the removal process of filter cakes in the below table. The Table 3 depicts a breaker with volume concentration of EDTA 35% being part of other concentrations like surfactant and Sodium Chloride. Table 4 shows the results of the treatment in removing filter cakes with EDTA inclusive. At a longer period of 90 hours, concentrated volumes of EDTA and other chemicals resulted in effectively removing the filter cakes.

Table 4. Filter Cake Breaker With 35% Vol of EDTA



Material	Unit	Quantity
65 pcf NaCl brine	Vol%	55
EDTA	Vol%	35
Surfactant	Vol%	10

Table 4. Effect of EDTA inclusive in Filter Cake Removal



Soaking time, hr	Disk #	Weight of Disk saturated in brine (W_1), g	Weight of Disk + Filter cake (W_2), g	Weight of Disk + Filter cake after the treatment (W_3), g	Removal Efficiency, wt%	Average wt%
24	1	44.611	60.468	53.375	44.73	40.33
	2	49.095	62.251	57.523	35.94	
42	3	48.52	61.218	53.474	60.99	65.76
	4	49.243	58.716	52.035	70.53	
90	5	49.448	60.392	49.771	97.05	97.05

2.10 Typical Mechanisms of Filter Cake Breakers

Breakers are seen as the lasting remedies to solving challenges relating to formation damage. This damage poses threats to well productivity and economic inclination [23]. Filter cake breakers are designed to work in wells that are completed in stand-alone liners or standalone screens and water injector open hole completion wells. It is intended to breakdown degradable filter cakes to support the removal process, and some of these compounds that can easily support the breaker mechanisms are magnesium citrate, magnesium tartrate, calcium citrate, calcium tartrate, calcium succinate, calcium malate and bismuth citrate [24]. Breakers such as chelating agents, enzymes and nanoparticles under surviving temperatures and pressures are also able to breakdown or dissolve filter cakes that contains starch additives; for the control of fluid-loss and calcium carbonate.

As shown in the Fig. 15 below, the filter cake breakers under review gives a more reasonable pH that is environmentally friendly to personnel and downhole equipment [25]

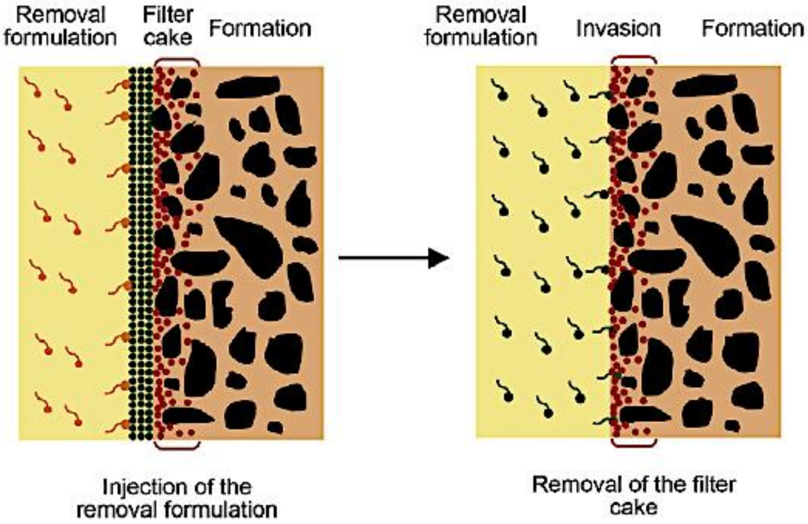


Figure 15. Filter Cake Breaker Mechanism

2.11 Theory of Return Permeability

Defining flow without resistance is the desire for most petroleum engineers with regards to formation damage. Al-Ibrahim [4], considerably developed a laboratory analysis pertaining to return permeability. The experiment sort to pass a rock assessment test under a temperature of 160°F and at a pressure of 2,000 psi; permeability at this stage was noted as the base or initial test. In Fig. 16 kerosene was said to have been injected at a rate of 3 cm^3/min whiles an observatory pressure drops over time were attained and recorded. A formulated breaker (made of EDTA and Surfactant) was subsequently injected in the counter direction of the base permeable rock at a rate of 0.1 cm^3/min, under same pressure and temperature. After successful 24 hours soaking period, the rock was assessed and again injected with kerosene to define return permeability. These experiments were seen necessary to appreciate the effect of the filter cake breakers in reservoir rocks.

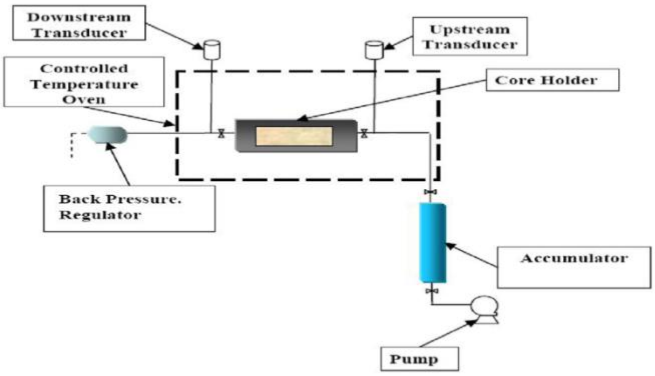


Figure 16. Core Flooding Test

2.12 Compilation of Authored Breaker Removal Efficiency

Fluid ingredients used for designing drilling mud can by far influence filter cake generation [26]. Kick prevention or keeping an overbalance formation should have weighting materials that consist of calcium carbonate, barite, ilmenite [27]. For the case of barite, this was earlier brought into existence in 1930 but the impediment was noticed in formate brines [28]. A greater proportion of drill-in-fluid design consist of weighting material; hence, the dissolution of these materials will give rise to removal efficiency. Authored researches are compiled for educative comparison.

Table 5. Filter Cake Removal Efficiency, [26]

Authors	**Weighting Material**	**Porous Medium**	**Breaker**
[29]	Barite	Ceramic Disc	Breaker: DTPA Eff.: 80%
[30]	Manganese tetroxide	Ceramic Disc	Breaker: HCl Eff. 100%
[31]	Calcium carbonate	Ceramic Disc	Breaker: MgO3 Eff. 75%
[32]	Manganese tetroxide	Ceramic Disc	Breaker: Lactic Acid Eff. 85%

CHAPTER 3

3. METHODOLOGY

The study of the thesis utilized a direct approach for conducting laboratory experiments, which included the formulation of biodegradable synthetic based mud drill-in-fluid, and subsequently building up filter cake from the BSBMDIF, under a breakthrough test. Chemical breakers were further composed using EDTA, SiO2, TiO2 and graphene as main component, for the treatment of BSBMDIF filter cakes. These treatments were followed up with soaking test, and to further identify the effectiveness of these breakers, an injectivity test was conducted to define return permeability, as shown in Fig. 17. All of the parameters were determined using weights, including the weight of the ceramic disc, build-up, and treated filter cakes. The treatment efficiency and return permeability over 24 and 42 hours, on the other hand, were all measured in percentages.

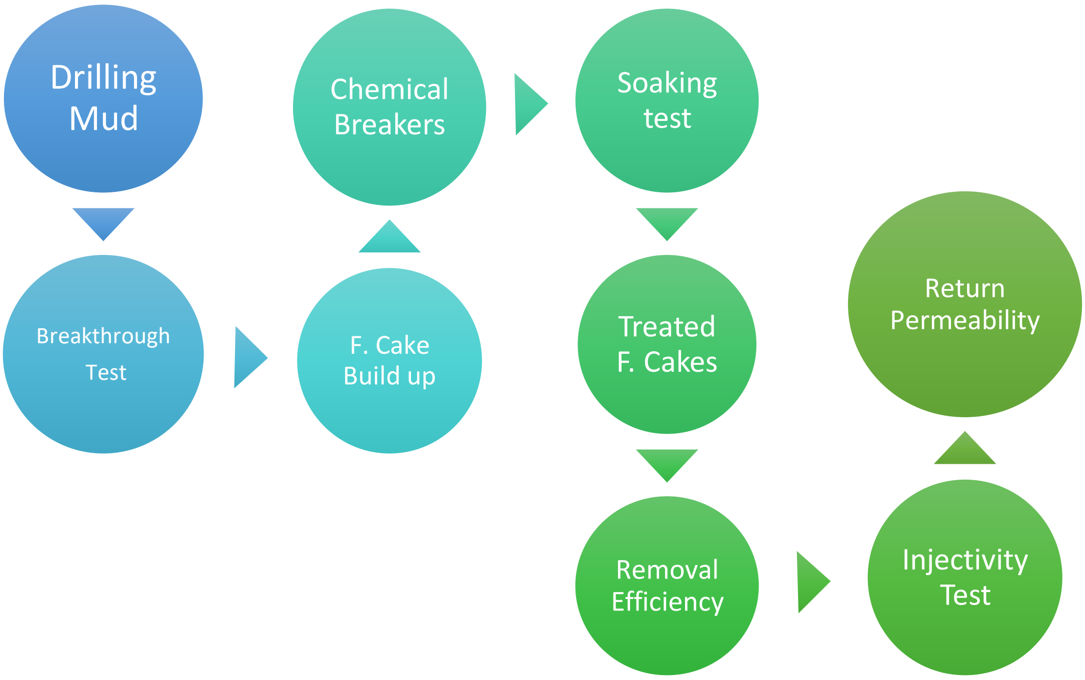


Figure 17. A structural flowchart of experimental procedures

3.1 Materials

$BaSO_4$, Barite is one of the industrial drilling fluid ingredients for fluid formulation. This was used in the laboratory as the main constituent of weighting material for the preparation of the drilling fluid, the particles of the barite were measured as $75\mu m$ [29]. Table 6. illustrates the formulation of drilling fluid. Barite, constituted 35.54% of the entire solids in the formulating weighed 3.54 ppg. Bentonite also constituted 0.24%, this viscosifier was used as an additive to help stabilize the well and carry cuttings to the surface [33].

Guar gum produced from guar beans and by the Indians are naturally safe. It's the first biopolymer that had proven itself environmentally friendly to both downhole equipment and personnel [34]. The biodegradable polymer considered for the experimental evaluation contained a fraction 0.12% in the biodegradable synthetic drill-in-fluid formulation. Its essence is to enhance the reduction of fluid loss and increase the potential cuttings carriage [35].

Calcium Chloride serving as a medium to cooling down the drilling bits and lubrication were used for the drilling fluid design with a component of 1.43%. This cost-effective fluid additive has the greatest potential for drilling shale formation [36] and it increases mud density to maintain overbalance in the wellbore [37]. Sodium Tridecyl Ether Sulphate was added to the fluid design, this emulsifier in the design acted as a fluid suspender where liquids were suspended in another. This type of surfactant constituting 0.71% was used to make fluids miscible [38].

A pH control additive was caustic soda, whose concentration was 1.43% in the formulation of the drilling fluid. This salt was added to maintain a pH that would keep away downhole equipment from rusting [39]. The powdery additive to controlling fluid loss was graphene. Graphene nanoplatelets with a concentration 0.24% had the tendency of increasing the plastic viscosity according to [40]. An industrial MG3 based oil fluid from PETRONAS constituting 46.26% was added to the fluid design with a 14.23% fresh water. The rheological properties of the drilling mud formulated is found in Table 6.

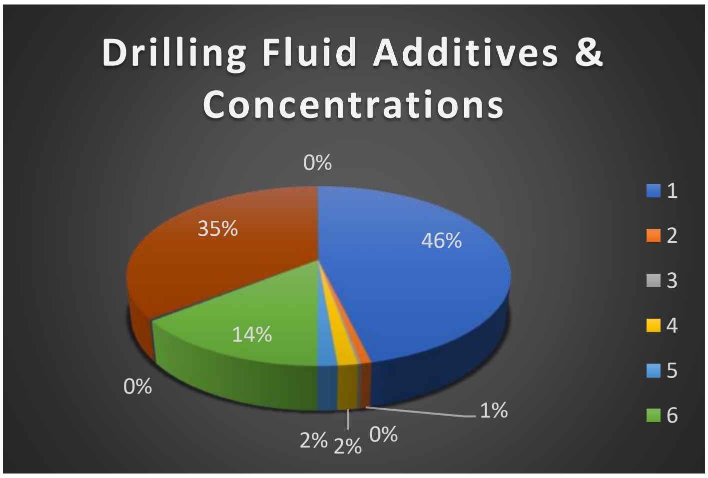


Figure 18. Fluid Additives & Concentrations

Table 6. Drill-In-Fluid Formulation

Additives		
	ppb	ppg
[1]Base Oil (Synthetic)	194.77	4.46
[2]Sodium Tridecyl Ether Sulphate (emulsifier)	3	0.07
[3]Bentonite (viscosifier)	1	0.02
[4]Caustic Soda	6	0.014
[5]Calcium Chloride	6	0.014
[6]Water	59.9	1.43
[7]Graphene Powder (Fluid Loss Control Agent)	1	0.02
[8]Barite (weighting material)	148.86	3.54
[9]Guar Gum (Biopolymer)	0.5	0.01
		10.0245

3.2 Equipment For Experiments

The drilling fluid laboratory equipment in Nazarbayev University were used to conduct this experiment.

High Pressure High Temperature filter press (OFITE brand) for defining or measuring fluid loss and building filter cakes was used for this study. This operation involves the regulation of pressure and temperature that imitates the actual reservoir conditions. At its peak, filter cakes are developed and filtrate volume is attained. The main component of the filter press is the heating jacket, a carrier cell and an inlet and outlet valves that aids in gas injecting and saving filtration respectively.

The means to determining the basic rheological properties of the formulated drilling fluid is an OFITE 900 viscometer. This rotational couette viscometer has a measuring chamber where drilling fluid is placed in, then the rotor is driven by the motor at a relevant speed. The bob finally generates torque and subsequently gives reading in an angular form [41].

Soaking test was conducted using Blue-M oven. This equipment has an axial uniform temperature air flow used for baking or drying (Blue-M lab oven, n.d.).

Figure 21. Blue-M Oven

Figure 20. HTHP filter Press

Figure 19. OFITE 900 viscometer

3.3 Procedure

3.3.1 Drill-In-Fluid Design

Biodegradable synthetic based mud drilling fluid additives and its concentrations listed in Table 6 were considerably formulated using the industrial acceptable API standards [43], whose mud weight constituted 10.02 ppg. A viscosity mixer made form Hamilton was used to blend all the components of the mud formulation [44].

Initially, 1.43 ppg of water and 0.014 ppg of caustic soda were mixed at the same time at about 5 minutes for better dissolution, subsequently, 4.43 ppg of MG3 synthetic base oil was mixed with emulsifier at times different from the initial mix for another 5 minutes. In addition, 3.54 ppg of barite, 0.02 ppg of bentonite, 0.014 ppg of calcium chloride, 0.02 ppg of graphene powder, and 0.01 ppg of biopolymer (guar gum) were further added to stir using the viscometer mixture for a total period of 45 minutes. This initial formulation was named as SBMDIF1. In addition, two separate fluid formulation mixings were done at different durations, with the SBMDIF 2 mixture lasting 30 minutes and the SBMDIF 3 formulation lasting roughly 35 minutes.

3.3.2 Rheological Test

There are several functions associated to drilling fluid design. A good fluid formulation suitable for carbonate reservoirs should have the tendency of keeping hydrostatic pressure in the drilling column constant and as well carry cuttings to the surface [44]. This test measured the rheological properties of the fluids formulated. It aimed to define the true behavior of fluids when pressure and temperature are applied. Under drill-in-fluid formulation flow and deformation, a digital OFITE viscometer model 900 was used for this study, the plastic viscosity, yield point and gel strengths of the separate three fluid formulations were attained at a temperature of 40 ^{o}C, and with a mathematical equation (1) and (2), the results were reaffirmed and tabulated in Table 7;

$$PV\ (cP) = \emptyset_{600rpm} - \emptyset_{300rpm} \tag{1}$$

$$YP\left(\frac{Ib}{100ft^2}\right) = \emptyset_{300rpm} - PV(cP) \tag{2}$$

On the same fluid, the gel strength test was performed. The sample was agitated for one minute at 300 RPM to ensure appropriate distribution. After that, the sample was left static for ten seconds before being swirled at three revolutions per minute. The 10 sec-gel strength was calculated using the bob's maximum deflection. The maximum deflection of the bob was used to calculate the 10 min-gel-strength after shearing the sample at 600 RPM for 30 seconds and stirring it at 3 RPM for 10 minutes [45].

Table 7. BSBMDIF Rheological Properties

		BSBMDIF$_1$	**BSBMDIF$_2$**	**BSBMDIF$_3$**
Property	**Unit**		**Range**	
Density	Ib/ft^3	120.02	120.02	120.02
PV	cP	97.0	93.8	95.9
YP	Ib/100 ft^2	136.4	133.4	135.3
10s gel	Ib/100 ft^2	2.8	2.5	2.7
10 min gel	Ib/100 ft^2	3.2	3.1	3.1
Fluid Loss	mL/30 min		<6	
Filter cake thickness	1/32 inch		<2	
pH			9 - 10	

3.3.3 Filter cake breaker formulation

The prospective filter cake breakers were all formulated in weights (grams) and contained 36.7% (45g) concentrations of EDTA, SiO2, TiO2, and Graphene in each of the four formulations. NaCl, Deionized Water, Surfactant (Dioctyl Sulf. Sodium Salt), and Mutual solvent (1-Butanol) were the additional components used in the formulation of each breaker, with concentrations of 20.43% (25g), 32.69% (40mL/g), 1.94% (2.38g), and 8.17% (10g), respectively.

Surfactant in the breaker formulations was seen to convert the emulsified synthetic filter cake to a more water-wet system which aided the easy flow of fluid to the surface of the rock [3].

1-Buatnol, a mutual solvent was added to the breakers to serve as oil dissolver. The environmentally friendly alcohol is 7% soluble in water [46]. Table 9 – 12 shows breaker formulations and concentrations.

Table 8. Breaker 1

Material	**Quantity**	**Vol%**
EDTA	45g	36.77
NaCl	25g	20.43
Deionized Water	40mL/g	32.69
Surfactant (Dioctyl Sulf. Sodium Salt)	2.38g	1.94
Mutual Solvent(1-Butanol)	10g	8.17
	122.38g	100%

Table 9. Breaker 2

Material	**Quantity**	**Vol%**
SiO_2	45g	36.77
NaCl	25g	20.43
Deionized Water	40mL/g	32.69
Surfactant (Disodium Salt)	2.38g	1.94
Mutual Solvent(1-Butanol)	10g	8.17
	122.38g	100%

Table 10. Breaker 3

Material	**Quantity**	**Vol%**
TiO_2	45g	36.77
NaCl	25g	20.43
Deionized Water	40mL/g	32.69
Surfactant (Disodium Salt)	2.38g	1.94
Mutual Solvent(1-Butanol)	10g	8.17
	122.38g	100%

Table 11. Breaker 4

Material	**Quantity**	**Vol%**
Graphene	45g	36.77
NaCl	25g	20.43
Deionized Water	40mL/g	32.69
Surfactant (Disodium Salt)	2.38g	1.94
Mutual Solvent(1-Butanol)	10g	8.17
	122.38g	100%

3.3.4 Filter Cake Build Up Test

Drilling operators and engineers are by all means possible finding an efficient way to preventing formation damage from occurring. The easiest way possible is by designing a good drilling fluid. This test was conducted using HTHP filter press and eight units of ceramic discs. At a temperature of about 200°Fand an initial pressure of 100psi [16] by injecting nitrogen gas, a carrier cell containing the designed drilling fluid on a ceramic disc was allowed to prepared. An increased pressure of 500psi was maintained whiles the lower valve of the HTHP filter press was opened to determine the rate of fluid loss over time. Fluid loss is a proof of wettability alteration due to invasion. After 3 hours of observatory filtration, the filter cake was ready and cake thickness and weight were measured and recorded.

3.3.5 Breakthrough Test

The very essence of this test was to determine the effect of breakers or solutions acting on filter cakes over time [29]. Similarly, the breakthrough time will indicate the time that the filter cake breaker solution would take to create passage or flow path through the filter cake formed. From Table 8-11, there are 4 different breaker concentrations (EDTA, SiO_2, TiO_2 and Graphene particles) designed to optimally break down the layered filter cakes or detach or degrade the biopolymers in the synthetic filter cakes. Whiles the HTHP filter press was considered for the test, each of the 8 filter cakes formed were placed in the carrier cell and 100ml breaker solution was poured into it. At a nitrogen gas injected pressure of 100psi and temperature of 200°F, the valve below the HTHP filter press was opened. Time for fluid produced was weighed and recorded as seen in Table 12.

Table 12. Breakthrough Test Results

Formulated Breaker	g/5mins	g/10mins	g/15mins
EDTA	33.82	27.08	3.42
SiO_2	41.20	12.52	4.70
TiO2	38.50	19.61	2.97
Graphene	23.89	31.84	1.2

3.3.6 Soaking Test

A direct effective interaction of the breaker solutions [32] to the filter cakes is what the soaking test sought to achieve. After the breakthrough test, the breaker solution was left to react with the filter cakes in a regulated oven with a temperature of 200°F. Each of the 4 breaker solutions (EDTA, SiO_2, TiO_2 and Graphene particles) under constant temperature observed a 24-hour and 42-hour soaking periods. Soaked cakes were removed from the oven and weighed.

3.3.7 Injectivity Test

Injectivity test was conducted so as to determine the efficiency of the filter cake breaker solution in removing the filter cake after long hours of soaking. The HTHP filter press was again considered for this experiment. The test included MG3 synthetic base oil, soaked filter cakes and nitrogen gas. Initially, a standard test was conducted using 200ml of MG3 base oil poured onto a ceramic disc in a carrier cell with a pressure of 20psi. The valve below the HTHP filter press was opened and the graduated cylinder was used to collecting the oil and recorded over time. This standard test was used as a benchmark for the actual test.

Each of the 8 filter cakes were now placed in the carrier cell and 200ml MG3 base oil was poured into the cell. A pressure of 20psi was injected and the below valve of the filter press was opened to observe the time of flow. The differences between the benchmark and the actual test were recorded and termed as *return permeability.*

3.3.8 Filter Cake Removal Test

Filter cakes had been successfully formed under a pressure and temperature of 500psi and 200°F respectively. This test was conducted to determine how much bridging agents and weighting materials had been reduced or damaged in the filter cakes. Before the filter cake build up, the ceramic disc was weighed alone and labeled W_1. After the cake build up, the cake on the ceramic disc is again weighed and labeled W_2. Breaker solutions acting on the filter cakes were allowed to soak for 24-hour and 42-hour, each of these were weighed and labeled as W_3. The concept of the removal test is by calculating the weight of these ceramic disc that had undergone several tests.

Let;

Filter Cake Removal Efficiency % = RE, %

Weight of ceramic disc = W1

Weight of ceramic disc after cake build up = W2

Weight of ceramic disc after breaker solution = W3

Hence,

$$RE,\% = \frac{W2 - W3}{W2 - W1} \times 100$$

3.3.9 Return Permeability Test

Formation damage due to reduced permeability in this experiment is a major challenge that represents the actual conditions in real situations [47]. Return permeability shadows remedies to increase the tendency of a free flow of formation fluids into the formation. Based on the injectivity test above, the return permeability is calculated by marking out the differences between the standard or benchmark to the final or actual as shown in Table 13 and 14.

Let;

Return Permeability % = RP, %
Initial Permeability (Benchmark) = K1
Final Permeability (Benchmark) = K2

By mathematical representation,

$$RP, \% = \frac{K2}{K1} \times 100$$

Table 13. Injectivity Test Results for 24 hours

Soaked filter Cakes + MG3 base Oil + N_2	**g/5mins**	**g/10mins**	**g/24hrs**	**Return K, %**
Injectivity Benchmark	166.45	114.39	280.84	100
EDTA, Cake 1	2.19	5.86	158.64	56.48
SiO_2, Cake 2	2.01	6.09	139.85	49.79
TiO_2, Cake 3	3.32	5.89	142.05	50.58
Graphene, Cake 4	1.98	4.88	129.02	45.94

Table 14. Injectivity Test Results for 42 hours

Soaked filter Cakes + MG3 base Oil + N_2	**g/5mins**	**g/10mins**	**g/42hrs**	**Return K, %**
Injectivity Benchmark	166.45	114.39	280.84	100
EDTA, Cake 5	6.92	9.59	210.34	74.89
SiO_2, Cake 6	4.12	5.32	149.22	53.13
TiO_2, Cake 7	4.70	4.96	144.67	51.51
Graphene, Cake 8	3.24	6.78	148.77	52.97

CHAPTER 4

4. RESULTS

4.1 Drill-In-Fluid Design

The drill-in-fluid was designed under careful chemical mixture combinations. The mud was formulated in 3 different scenarios and had undergone a rheological property and fluid loss test.

The potency of the mud to carry cuttings or suspend cuttings while drilling was calculated by finding the ratio of the yield point to plastic viscosity. The common range for mud cutting suspension is in the range of 0.75-1.5 [44]. From the experiments, all the three tested biodegradable synthetic based mud drilling-in-fluid formulated, fell within the range with an approximate value of 1.413.

DIF 2 proved better than the rest as shown in Fig. 22 as it had 94.8% reliability to suspend cuttings.

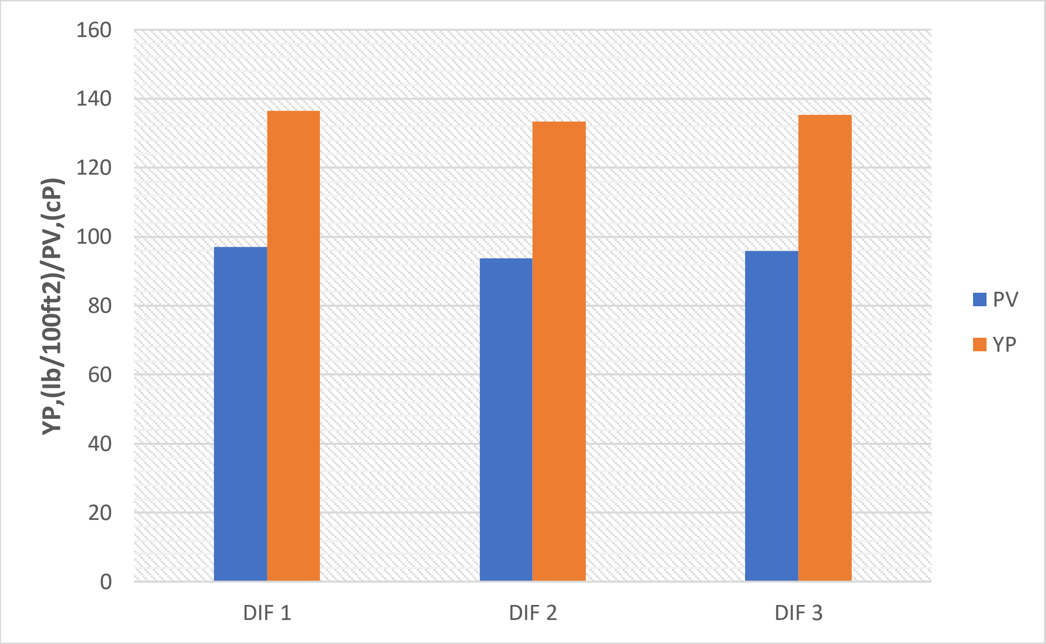


Figure 22. Ratio of DIF's Yield Point to Plastic Viscosity

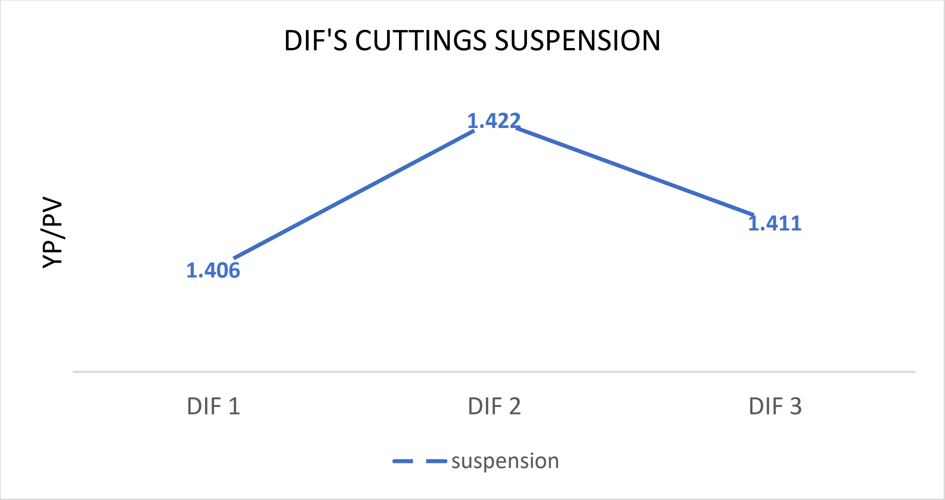


Figure 23. The capacity of DIF's to carry or suspend cuttings during drilling

At static conditions, the experiment sought to have defined the conditions of suspending cuttings while drilling in HTHP reservoirs. To simply understand, the induced shear stress was made to be still for 10 seconds and 10 minutes with references to API standards. After a while the values preceding was recorded. The disparities against 10s gel strength were seen to have changed throughout DIF 1, 2 & 3. Whiles the 10mins gel strength for DIF 1 changed, the others remained constant. All these were influenced under an average yield point of 135.03 Ib/100 ft^2.

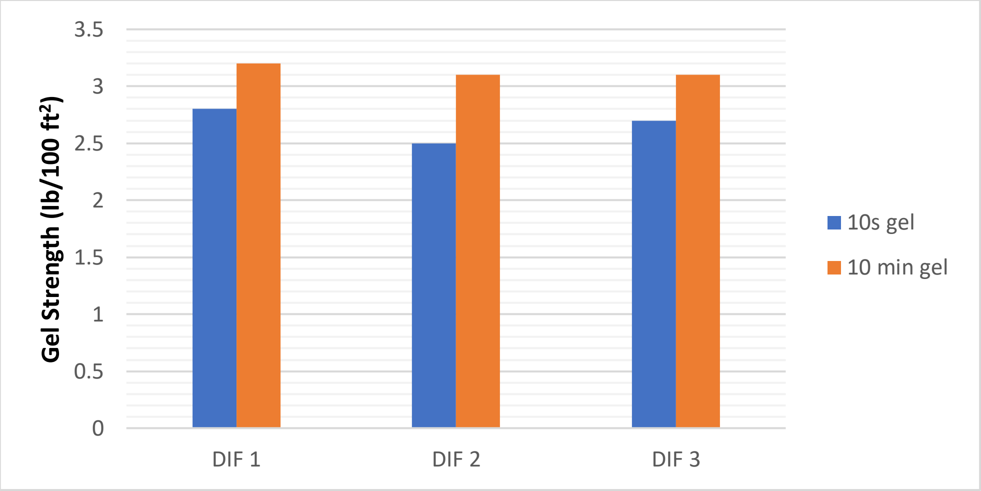


Figure 24. DIF's Static Cuttings Suspension

Identifying the rate of invasion of drilling fluids into the reservoir was experimented by pouring the well-designed biodegradable synthetic based mud drill-in-fluid onto a ceramic disc in a carrier cell and further heating and pressuring it in a HTHP filter press. The rate of flow of fluid from the outlet of the filter cake press was recorded and defined as fluid loss. The differences between the DIFs were negligible from the beginning, but after 3 hours of continues nitrogen gas injection, the fluid loss for all the three DIFs shot up to an average of 39.6 ml. From Fig. 24, a filter cake was built up, and the weight and thickness for all were measured and recorded under Table 7.

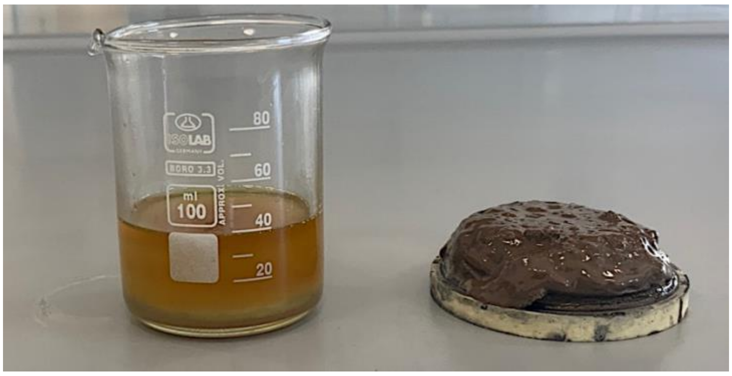


Figure 25. Fluid Loss after 3 hours N2 Injection

4.2 Filter Cake Breakers

Well completions are essential for hydrocarbons to flow from the reservoir to the wellbore. The experimental analysis conducted required means of degrading weighting and bridging agents in the biodegradable synthetic based mud drill-in-fluids. The means to do this was to evaluate the strength of Ethylenediamine tetra acetic acid, silica dioxide, titanium dioxide and graphene particles. Table 8-11 shows the exact concentrations used for the experiment.

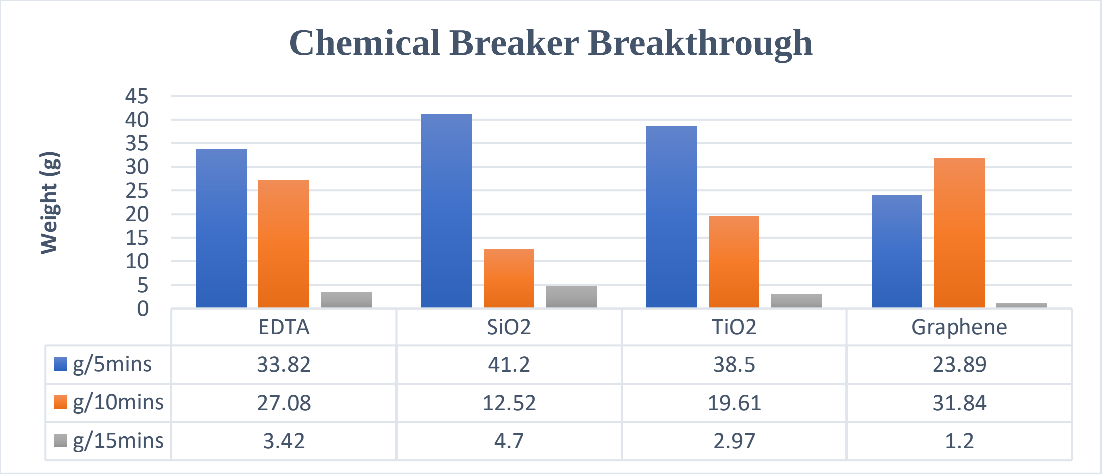
Considering the rheological properties of the biodegradable synthetic based mud drill-in-fluids, an eight-filter cake was built to undergo contact reactions with the breaker solutions prepared. Using the HTHP filter press, the breaker solution was poured into the carrier cell. A regulated temperature and pressure were induced into the press for contact reactions. The time for the passage to be created for the breakers to pass through the filter cakes were observed, timed, weighed and recorded. At g/5mins, SiO_2 was seen to be the fastest to breakthrough because the evenly dispersion of the silica were forced to detach the weighting materials present in the filter cake. At g/10mins, graphene particle was seen to have recovered much better than the rest and finally at g/15mins, SiO_2 did again breakthrough early.

Figure 29. 100ml TiO2 Breaker [Stirred for 30mis]

Figure 28. 100ml EDTA [Breaker Stirred for 30mis]

Figure 27. 100ml Graphene Breaker [Stirred for 30mis]

Figure 26. 100ml SiO2 Breaker [Stirred for 30mis]



	EDTA	SiO2	TiO2	Graphene
🟦 g/5mins	33.82	41.2	38.5	23.89
🟧 g/10mins	27.08	12.52	19.61	31.84
⬜ g/15mins	3.42	4.7	2.97	1.2

Figure 30. Chemical Reactions of Breakers to Filter cakes

According to the data in Fig. 30, the test was called off after 30 minutes of continuous nitrogen gas injection because of no breaker solution was present in the carrier cell.

In addition, breaker solutions were placed under the eye to observe the solubility of the breaker solutions to the filter cake. A considerable amount of the filter cake was placed into a plastic container and breaker solution added. A gentle mix was done in Fig. 31 & 32, and under observation, EDTA was noted soluble, but SiO2 was not but there were separations; this is because the molecules were not soluble to the DIF.

Figure 32. EDTA + DIFs = Soluble

Figure 32. SiO2 + DIFs = Separation

4.3 Filter Cake Removal Test

The initial weight of the filter cake buildup on ceramic disc was considered and the weight of the soaked or treated filter cakes after a period of 24 and 42 hours were recorded. The blue and orange bars on the chart indicates the effective dissolution of barites and bridging agents from the filter cakes with respect to time. The lesser the weight, the more effective removal.

EDTA at 24 hours and 42 hours dissolved all the weighting and bridging materials within the filter cakes. The weight was compared to the other nanoparticles whose removal efficiency were lower as demonstrated in Fig. 33.

Table 15. Evaluating Breakers in Removing SBMDIF

Chemical Concentration	Soaking Time, Hrs.	Ceramic Disc #	Weight of Ceramic Disc, w1 (g)	Weight Disc + Filter Cake, w2 (g)	Weight after treatment, w3 (g)	Removal Efficiency, weight %	Return Permeability, %
EDTA	24	1	41.66	72.10	52.12	65.64	56.48
SiO_2		2	41.60	71.30	55.20	54.21	49.79
TiO_2		3	41.66	74.10	57.00	52.71	50.58
Graphene		4	41.68	72.60	61.09	37.23	45.94
EDTA	42	5	41.66	75.10	48.02	80.98	74.89
SiO_2		6	41.71	72.10	51.09	69.13	53.13
TiO_2		7	41.67	72.09	54.00	59.47	51.51
Graphene		8	41.56	75.10	60.40	43.83	52.97

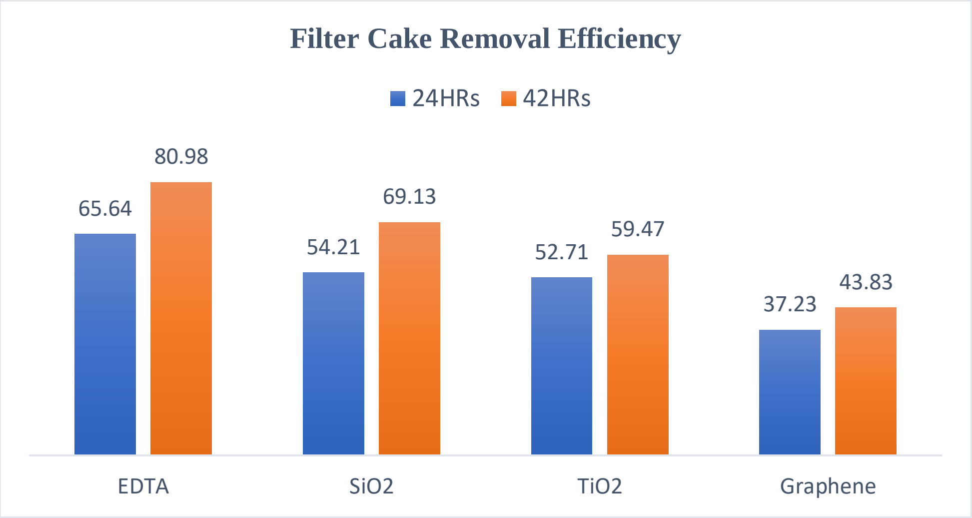


Figure 33. Removal Efficiency

4.4 Return Permeability

The filter cakes that had undergone different types of treatments were tested to evaluate the capability of retaining or maintaining maximum permeability effect. Under a pressure of 20psi, a ceramic disc and 200ml of synthetic base oil was observed by opening the outer valve of the HTHP filter press to flow, as demonstrated in Fig.33. This experiment recorded by the weight and time of flow and was indicated as the benchmark to support the test for the actual.

Figure 34. Permeability Standard Test

All eight treated filter cakes on ceramic disc were placed in the carrier cell with 200ml of MG3 base oil and same pressure of 20 psi was applied. From Fig. 34, the result of the experiment indicated that, ethylenediaminetetraacetic acid breaker solution gained better grounds to allow the flow of MG3 base oil through the filter cakes at 24 and 42 hours. However, at a longer period of time, nanofluids were also gaining momentum.

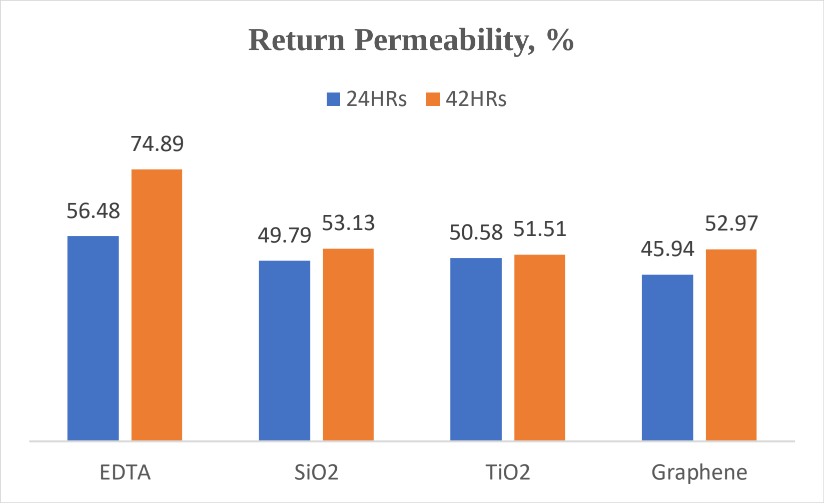


Figure 35. Return Permeability after filter cake treatments

4.5 Breaker Evaluation

The relevance of the curve is a determinant of an effective breaker under the filter cakes experiments conducted. The curve, is a demonstration of filter cakes removal efficiencies versus the tendency of the treated filter cakes to gain or return permeability. The curve in Fig. 36 states that, the greater the return permeability of the treated filter cakes, the greater the removal efficiency. Hence, RP% is directly proportional to RE% [4].

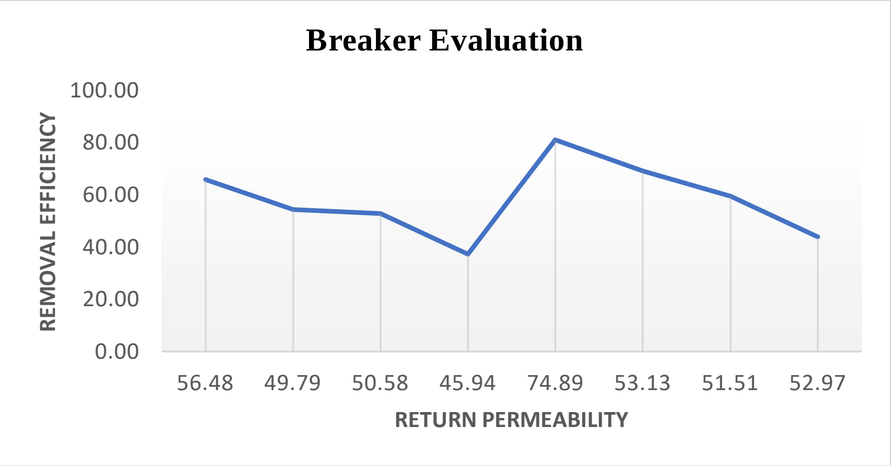


Figure 36. Breaker Evaluation

CHAPTER 5

5. CONCLUSIONS AND RECOMMENDATIONS

Pertaining to the objectives of the study, the underlisted are the conclusions;

i. In reference to API standards, an effective BSBMDIF was formulated to weigh 10.02ppg. Under the rheological property test, all the three DIFs experimented were in the range of stabilizing the wellbore and had the capacity of suspending and carrying cuttings. The average ratio of yield point to plastic viscosity of 1.413 was under the acceptable range of 0.75 -1.5 [44].

ii. Breaker 1, 2, 3 and 4 were interchangeably used for the main breaker constituents EDTA, SiO_2, TiO_2 and Graphene particles. EDTA from breaker 1, was noted to have efficiently removed the biodegradable synthetic based mud DIF filter cakes at 65.64% after soaking with breaker 1 for 24 hours, and at 80.98% after soaking for 42 hours. More so, the effect of longer periods of soaking filter cakes had a greater influence on the removal efficiency, hence, the longer the periods of soaking, the higher the removal efficiency.

iii. Breaker 2, 3 and 4, which were silica dioxide, titanium dioxide and graphene particles did not dissolve the weighting materials in the filter cakes, but was able to degrade the presence of guar gum, and for this reason, silica dioxide had consistent amount of flow after 30 mins of breakthrough test than the rest of the breakers.

iv. Filter cakes from the biodegradable synthetic based mud drill-in-fluid that were treated with EDTA and nanoparticles achieved an efficient result under return permeability (RP) test, the breakers were valued in percentages as EDTA after 42 hours topped with the highest RP% of 74.89%, while graphene had the lowest RP% of 52.97% at same soaking hours.

v. The nanoparticles were able to withstand harsh temperatures and pressure conditions for over 100 to 500 psi and 200°F during the period of breakthrough and soaking test, as the physiochemical structures of the nanofluids remained intact.

This study seeks to recommend the following for onward research activities;

i. 10 grams each of silica dioxide and EDTA can be put together to formulate a breaker solution with other concentrations for the effective removal of filter cakes in the near future.

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