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Self-Diverting Nanofluid In-Situ Gelled Acid for Matrix Acidizing Applications in Carbonate Formations

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SELF-DIVERTING NANOFLUID IN-SITU GELLED ACID FOR MATRIX ACIDIZING APPLICATIONS IN CARBONATE FORMATIONS

A Thesis

by

JAVIER ALEJANDRO PEREZ

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May 2022

ABSTRACT

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Matrix acidizing is a very common technique used to improve the recovery from sandstone and carbonate reservoirs. One of the most popular nanoparticle for matrix acidizing applications is silicon dioxide. This nanoparticle produces diversion by forming an in-situ gelled acid in carbonate reservoirs using specialized fluids. Some parameters that influence in the formation of a gel such as pH, volume concentration, and the addition of a surfactant were analyzed in this project. The main goal of this research was to determine optimum conditions for a matrix acidizing using the nanobased stimulation fluid. Among the parameters studied in this research are the vol % of silica nanoparticles, the effect of an anionic surfactant and the effect of salt.

All the investigations regarding these parameters were performed in the lab. These experiments were separated in two categories. Bench top experiments and coreflood experiments. The bench top experiments were reactions with different components in which different parameters such as pH and concentration of reactants were studied. Then, the coreflood experiments were performed, in which the best results from the bench experiments were used only.

Twenty-five mL samples were prepared with hydrophobic silica nanoparticles and surfactant Bioterge AS-40 with a total nanoparticle concentration of 2.5 vol % with 97.5 vol% deionized water and 4 wt% NaCl. Some of the samples were made without surfactant and some without salt. The samples were mixed with vortex and used a horn sonicator with 25% amplitude for 20 minutes. The pH of the sample was adjusted using 10 vol% NaOH and 10 vol% HCl solutions. Independent samples were prepared for each pH value tested to avoid dilution in the nanoparticle gel via addition of further NaOH or HCl solution. These experiments were executed in triplicates to get more accurate results. In this set of experiments, the pH range was adjusted to about 1.5, 3, 7, 11 and 12.5. Based on the results that were gathered, two different fluids were selected for the coreflood experiments. The first fluid (test A) consisted of only 15% HCl, the second fluid (test B) 2.5 vol % silica nanoparticles with 4 wt% NaCl and without surfactant AS-40. The third fluid (test C) consisted of 2.5 vol % silica nanoparticles with 4 wt% NaCl and 17 wt% of surfactant AS-40. The coreflood experiments consisted in injecting the fluid with acid at high pressures to a core sample using a coreflood apparatus.

During the coreflood experiments it was found that the best pH is between 7-10, the viscosity value is between 300-350 centipoise, the volume concentration is 2.5 vol% silica nanoparticles and the addition of a surfactant was found to have very close values of viscosity, gelation, pH range with the difference that slightly higher viscosities were found. Unfortunately, the nanofluid containing surfactant (test C) could not be used for the coreflood experiments. A nanofluid made with 2.5 vol% silicon dioxide nanoparticles in deionized water, 4 wt% NaCl and 15 wt% HCl was injected into Indiana limestone. The propagation of the fluid through the rock was investigated and found to be successful using the transducers and by observing the wormholes produced in one of the core samples after injection.

DEDICATION

Me gustaria dedicar esta tesis principalmente a mis padres Francisco Javier Perez Pena y Luz Esthela Olivares Sainz por ser el mejor ejemplo de gente exitosa, ejemplar, muy trabajadora. Todo lo que he logrado es gracias a ellos, por el inmenso apoyo economicamente y mucho mas importante emocionalmente. Gracias por todo lo que han hecho por mi, por siempre estar ahi para apoyarme, para hacerme entrar en razon cuando estoy mal y para inculcarme de una manera ejemplar, es lo mas valioso que me pueden ensenar. Tambien agradezco a toda mi familia (mis abuelos, tios, amigos) que me han apoyado a lo largo del camino, todos han sido de gran ayuda. Agradezo todo el amor y el carino de ellos hacia mi.

I would like to dedicate this mainly to my parents Francisco Javier Perez Pena and Luz Esthela Olivares Sainz who are the best example of successful, hard working and kind people. I thank them because everything I have achieved is mainly because of them. They have been supporting me extensively in the economic and more important emotionally, showing their love and their caring for me. Thank you for your lessons in life, it is the most valuable thing you can teach me. For overall, teaching me how to be the person that I am now. Also, I would like to dedicate this to my family (grandparents, uncles, aunts and friends) I thank you all for your support and your love.

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CHAPTER I

INTRODUCTION

Goal

The main purpose of this project is to develop a nanofluid system that would help to divert the injected acid from the main flow regime into a relatively lower permeability zone and being able to dissolve the rock significantly. The system is meant to successfully create acidic gel in-situ after injecting the fluid in solution. It is expected that by altering either pH, temperature or amount of reactants, the viscosity of the fluid can be controlled so that the gel can be broken at a desired time.

Nanofluids

Nanofluids are defined as a type of fluids that are obtained by dispersing and stably suspending very small particles with the dimensions typically from 1-100 nanometers[1,2]. They are a new class of nanotechnology based on heat transfer fluids which are found to have superior properties such as having an increased thermal conductivity and heat transfer when compared to conventional fluids. Nanofluids are widely used by engineers in many different applications[1,3,6,7]. Some of the most common applications are industrial cooling applications, smart fluids, nuclear reactors, extraction of geothermal power and energy sources, automotive applications, etc. They can be formed from single nanoparticles such as Ag, Cu and Fe, single oxides such as Al_2O_3,

CuO, Cu_2O and TiO_2, alloys such as Ag-Cu, Fe-Ni and Cu-Zn, multi-oxides such as $NiFe_2)_4$, $ZnFe_2O_4$ and $CuZnFe_4O_4$, and carbon materials such as diamond, carbon nanotubes and graphite[2,6,18].

Nanofluids are classified into two main categories: single nanofluids or hybrid nanofluids. Single nanofluids are composed as a single type of nanoparticle whereas hybrid nanofluids are made in a combination of more than one type of nanoparticles. There are many methods for preparing nanofluids which would impact in the uniformity of the particle dispersion depending on the thermophysical properties that are planned to achieve. However, preparing nanofluids is often a complicated process since nanofluids are not made from conventional mixtures but they require special conditions such as physical and chemical stability, dispersibility, homogeneity, etc. There are two main methods to produce nanofluids, by using a single-step approach or a two-step approach[3,5,12]. Even though there are several applications in which nanofluids can be employed, one that is very important for the petroleum industry is when nanofluids are employed for matrix acidizing techniques to the oil in carbonate reservoirs. The reason is because by using nanoparticles there is a higher magnitude of interaction or reactivity between adjacent surfaces than using conventional particles, which makes it more beneficial for this application since it enhances the properties of the fluid basically using less amount of the material and since the nanoparticles are significantly smaller in size there is an easier transportation through the pores. In general, the most popular nanofluids used in the oil and gas industry are found to be nanosilica (SiO_2) and aluminum oxide (Al_2O_3) since they have a high potential and productivity in these applications[4]. Researchers have found that these nanoparticles not only improve the thermal stability of the drilling fluids, but they also have a positive impact on the rheological and filtration characteristics of the fluids[3,6].

Table 1. Typical nanoparticles employed in oil treatments[3].

Investigated Nanoparticles	Improved parameters	Reference
Aluminum oxide	Reducing oil viscosity for acidizing applications	7
Titanium dioxide	Improving the stability of the injected water for EOR applications	7
Aluminum oxide	Improving oil recovery using low salinity how water (LSHW) injection with addition of nanoparticles for EOR applications	8
Silicon dioxide	Improving oil recovery using low salinity how water (LSHW) injection with addition of nanoparticles for EOR applications	8
Aluminum oxide	Improving the rheological properties of the injected water for EOR applications	9
Silicon dioxide	Improving the rheological properties of the injected water for EOR and acidizing applications	9
Titanium dioxide	Improving oil recovery for EOR applications	9
Cellulose nanocrystals (CNCs)	Conformance control/ Stability of oil in water emulsions for fracturing	10
Graphene oxide	Reducing oil viscosity for EOR and acidizing applications	11
Graphene oxide	Reduction in oil viscosity/ Increasing oil recovery for EOR applications	11
Graphene-based zirconium oxide nanocomposite	Reducing excess water production for EOR applications	12
Magnesium oxide	Altering wettability for EOR applications	13
Aluminum oxide	Reducing interfacial tension for EOR applications	13
Zinc oxide	Reducing oil viscosity for EOR applications	13
Zirconium oxide	Reducing mobility ratio for EOR applications	13
Tin oxide	Altering permeability for EOR applications	13
Iron oxide		13
Nickel oxide		13
Hydrophobic Silicon dioxide		13
Nickel oxide/ Silicon dioxide	Enhancing oil recovery at low concentration for acidizing applications	14
Janus nanoparticles	Reducing formation damage/ Reducing interfacial tension, hence increasing oil recovery for EOR applications	14
Polymer-coated nanoparticle	Improving mobility control, altering surface wettability for EOR applications	15
Silicon dioxide	Increasing sweep efficiency/ Improving foam stability for alpha-olefin sulfonate (AOS) solution for acidizing	16
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Table 1 has the most common nanofluids that are employed in oil treatments and applications. As it is seen in the table, silicon dioxide it is one of the most effective in oil recovery and acidizing. These types of nanoparticles have been found to be very helpful in the last decade and it is expected that they would be more useful even in more applications as there is a lot of room to improve.

It is of extreme importance to understand how nanofluids influence in the overall effectiveness of oil treatments such as matrix acidizing. Engineers are aware of the importance of controlling the viscosity of nanofluids since this would help greatly in the final output for the system. In such treatments, working with silicon dioxide or aluminum dioxide is very common since they have been shown to work good in acidizing techniques. Furthermore, if engineers are capable of controlling the viscosity of the nanofluid system it is highly believed that the overall effectiveness of such treatment would be greatly improved[,5,16].

Carbonate Reservoirs/ Matrix Acidizing Technique

Carbonate reservoirs have heterogeneous properties in vertical and horizontal directions, with large permeability barriers, natural fractures, and many porosity types[3]. The matrix acidizing technique is employed to enlarge or create wormholes typically using hydrochloric acid due to is low cost and high dissolution into the carbonate rock[4,7,15]. Carbonate reservoir faces continuous diagenesis due to high pressure increase on burial and results into physical compacted and natural fractures[5]. These fractures are further increased by completion processes and drilling. The complexities found in carbonate reservoirs increases the problem for fluid flow. Matrix acidizing is used to improve the flow rate through dissociation of the reservoir rock and to enhance reservoir conductivity by injecting an acid stimulated fluid to the reservoir rock just below fracture pressure[3,5,8,14].

Acids

In the oil industry acids are widely used due to their important task in well stimulation operations. Acids can increase well productivity by dissolving material such as minerals, drilling mud, etc. There are three different acidizing techniques: acid fracturing, matrix acidizing and acid washing[4]. In the selection of an acid there are three main chemical factors that are analyzed before the reaction takes place. These are reaction rate, equilibrium and stoichiometry[4]. It is required to know how many moles of the acid are needed to complete the reaction with reservoir materials[5]. One of the most used acids is hydrochloric acid because is economic and such as a strong acid that fits perfectly in the acidizing techniques. The chemical reactions of HCl with dolomite and calcite are shown below:

Hydrochloric acid

HCl reaction with Calcite:

2HCl + CaCO3 ---> CaCl2 + H2O + CO2 (1)

HCl reaction with Dolomite:

MgCa(CO3)2 + 4HCl ---> CaCl2 + MgCl2 + 2H2O + 2CO2 (2)

There are different types of acids that can be used to maximize the efficiency of the stimulation processes for example organic acids, retarded acids, mineral acids, powdered acids, emulsified acids, viscoelastic acids and gelled acids[2,11,16]. A good example of a mineral acid is HCl, which has been found that a solution of 10-15 wt% HCl is widely used in many carbonaceous formations and in sandstone stimulation. However, one limitation of the HCl is that it has a very high corrosivity which is a problem specially at very high temperatures since it produces damage to the equipment[2,13,22]. Some organic acids unlike HCl, have a lower corrosivity for example formic acid and acetic acid. These acids can be used for other applications with longer contact with the equipment avoiding the damage[2,6,13]. However, organic acids have a retardation effect and low degree of corrosivity, they dissolve the rock at a much slower rate compared to HCl and sometimes is difficult to penetrate the wormhole leading to insufficient stimulation of formation. Even though HCl is said to be the best acid used in these applications, there are some cases in which it is not the best option. This is because sometimes because of the rapid interaction between the carbonate and HCl limits the penetration of the acid into the formation, especially if the pumping rate is very low. Also, HCl is very corrosive and the corrosion inhibitors can only protect the tubulars at high temperatures for a very short period, not to mention that these inhibitors are very expensive. In some cases, a mixture of HCl with an organic acid leads to a perfect balance of the fluid and can achieve productivity enhancement penetrating the wormhole with enough stimulation and a good degree of corrosivity[5,8,15]. Some examples of organic acids are formic acid, citric acid and acetic acid which are often used for matrix acidizing applications. In a study using acetic acid for matrix acidizing in carbonate reservoirs revealed that the acid breakthrough volume for acetic acid was higher than that for hydrochloric acid and that the radius of the wormholes was bigger when using acetic acid at optimal rate. However, at low temperature, there was a lot of acetic acid required to propagate the wormholes when comparing to HCl. Based in this study, it is predicted with linear modeling work that at higher temperatures though, using acetic acid in some situational cases would be more efficient than using HCl since the reaction rate is higher[6].

Retarded acids are not as popular but still very useful in some applications that need a slower rate of reaction. These acids are used mainly to decrease the reaction rate between the acids and the rock. Some examples are retarded hydrofluoric acid, aluminum chloride and phosphonic acid. The problem with these acids is that they are not effective at high temperatures as they form precipitates in the reaction. Other very important type of acids are emulsified acids which are very popular in the oil industry due to their delayed nature that leads to a deeper penetration into the formation which facilitates the process of enhancing the well productivity with a low degree of corrosivity[7]. The issue with emulsified acids is that they don't work well in sandstone reservoirs. Some powdered acids are also used in these applications such as sulfamic and chloroacetic acid. Another type of acids are viscoelastic acids which are self-diverting acids that maximize the zonal coverage in carbonate reservoirs by viscosifying and stimulating the carbonate formation diverting the fluid into low permeability zones. Among the mentioned acids, cost per dissolving power is a very important factor that increases from acetic acid to formic acid and then to hydrochloric acid[4]. In order to design the best acid for every operation some factors such as temperature, cost, corrosivity, mineralogy, penetration and efficiency need to be analyzed carefully.

This nanoparticle system is in the classification of retarded acids. Therefore, the nanoparticles selected for our system must build viscosity in order to create the gel. There are some ways to increase viscosity in the fluid. In some cases, adding a surfactant to the acid-fluid solution would enhance viscosity and therefore creating the gel easier. When the nanofluid is injected at a high pressure, the acid-fluid mixture starts to react with the rock and therefore increasing the pH as the reaction proceeds. At this point is when the gel should start to build. The most important concept in order to create gelation is that there must be a reaction between the hydroxyl groups of the nanoparticles with water molecules[7]. This system strongly depends on pH, once the system reaches the pH needed, then the gel is created. This gelation process is created when the pH range is from 4-8[7]. Once the nanofluid system has been spread uniformly through the pores the next step involves breaking up the gelled acid. There are many ways that this gel can be broken for example applying intensive shear rate, increasing the temperature or changing the pH of the solution. Different type of acids are shown in table 2. It has been observed that retarded mud acids, organic-HF acids, single stage acids and 10% acetic acid are some of the common acids that are employed in acidizing applications. They have their advantages and disadvantages as it can be seen in the table, but they all are proved to work in their respective applications[4,7,18].

Table 2. Summary of acids employed in oil treatments.

Type of acid	Advantages	Disadvantages	Applications
Retarded mud acids	Reduces the reaction rate for penetration	Formation of precipitates at high temperature	Acidizing, EOR and fracturing
Organic-HF acid	Less corrosion rate, useful in HCl clay	Expensive, sometimes forms precipitates at high temperatures	Acidizing, EOR and fracturing
Single stage acid	Eliminates the use of pre-flush and after flush	Expensive	Acidizing, EOR and fracturing
10% acetic acid	Good results at high temperatures	Only applicable with high carbonate percentage	Acidizing, EOR and fracturing
Emulsified acid	Slow reaction rate and good stability at high temperature	Not applied on sandstone formation mechanisms	Acidizing, EOR and fracturing

Diversion

Diversion is an important step in the overall effectiveness of matrix acidizing techniques. It is basically the way the acid is transported through the pores of the reservoir. For an outstanding performance, a uniformly diversion of the nanofluid is expected. There are two main methods in which diversion can happen, a mechanical based method or a chemical based method. For example, some mechanical approaches would be using ball sealers, coiled tubing, squeeze packers or opposed cup packers[9]. The mechanical route is very practical, has its benefits but also its limitations. For example, it has a very high rate of water production bug also entails much higher losses due to friction and if the pressure is increased that only results in an injection rate reduction[5]. However, this research paper is more involved in chemical diversion techniques. Some of the most common chemical approaches are using in-situ gelled acids, gelled acids, emulsified acids, organic acids and viscoelastic acids.

Mechanical Diversion

Mechanical diversion techniques are a very common way to employ acid treatments to oil. There are several methods for fluid diversion for example; mechanical isolation by ball sealers, packers, diverting agents such as benzoic acid flakes or soluble resins. These types of techniques are very useful especially for their simplicity. Many advantages such as volume and duration of job, cost wise, good distribution in low permeability zones, good rate, etc. are found using this approach[2,6,14]. Mechanical diversion is said to be the most positive method of diversion simply because each stage of the treatment is found to act only on a concealed zone. However, is not always possible to employ this technique efficiently, large area of perforation with large intervals are difficult examples of operation for this technique due to the widespread area involved in those cases[2,4]. Also, moving around all the equipment used for packing during the operations could cause leaks and further problems.

Chemical Diversion

Organic acids are very popular, for example formic acid and acetic acid, they have a low degree of and are very stable even at very high temperatures. These two acids have a low viscosity and can be employed for small permeability contrast ratios applications in multilayered zones, they are also less expensive when compared with hydrochloric acid. However, there is no surprise that the latter is the most widely used acid in these applications due to its cost of acid per unit and dissolving power. Even though is a little more expensive than acetic acid and formic acid, hydrochloric acid can be used in a lot more applications.

Another common technique previously mentioned is using an in-situ gelled acid. This technique is based in an injection in which many compounds are involved, it could be a polymer in order to increase the viscosity of the solution so that a gel can be eventually formed, a crosslinker such as ferric chloride in order to increase viscosity at a low pH of 2, a breaker such as sodium erythorbate which could be used to reduce the viscosity by reducing the ferric ions to ferrous ions (opposite of crosslinker), and a corrosion inhibitor such as hydroxyacetic acid which degrades the polymer by removing the metal ions and overall reducing the viscosity[12,18]. Enough data shows that this approach is effective in most cases, but it could cause a loss in permeability in tight carbonate cores due to a gel retention produced by the polymer at the core face[15]. The next approach involves using viscoelastic (VES) acid systems, this type of system has the advantage of producing high viscosity by linking the polymer chains with micellar structures. However, this system requires an exact control of pH to work, is essential for achieving desired results. When working with low pH values, viscosity is low, this allows the acid to be distributed freely through the pores and to penetrate the matrix. When the pH is increased, the reaction of the acid with the carbonates is speed up and the concentration of the divalent ions end up increasing. At the end the viscosity ends up being increased because the micellar structures associate with the divalent ions. The problem with this approach is that the viscosity can be reduced significantly if there is a contact with hydrocarbons. This is a significant problem specially if the treatment is being done to dry-gas wells[12]. Lastly, the use of emulsified acids was very commonly used in oil treatment. This approach uses HCl as a internal phase for the emulsion and diesel as the external oily phase, this creates a diffusion barrier and promotes deep wormhole formation. However, in order for this approach to be successful there is necessary to have a diverting agent stage and a special treatment for the emulsified acid in treatments with heterogeneous or large permeability contrast formations. Also, a significant disadvantage found is that when the concentration of the corrosion inhibitor increase, especially at very high temperatures, the emulsion stability is reduced drastically[9].

In general, metal oxide nanoparticles are the best gelling agent for dispersion in the system[2,6]. This nanofluid is the best in diverting the acid from a high permeability zone into a low permeability zone and in deep penetrating the wormholes into the samples. It is arguably believed that in order to create a strong gel, there has to be a reaction between the cations and the hydroxyl groups found in the surface of the silica nanoparticles, especially if the cations are in an aqueous solution[2,5,14].

This reaction produces densely charged particles, the sign and the magnitude of these particles are strongly dependent of pH solution and the quantity of ions that are present. This acidizing treatment is implemented to avoid formation damage to the producing wells by dissolving the contaminants. For this treatment to be effective, one of the crucial parts of this process is diversion. Developing a suitable nanofluid system can drastically retard the dissolution of the surface of a rock and manage to penetrate deeper the acid treatment under different subterranean condition scenarios[7,11].

Gelation

The use of chemical diversion systems in acidizing techniques have been very common lately due to their success in different applications. However, detailed knowledge on the particle size distribution of the system and the downhole configuration needs to be achieved in order to be efficient. The formation of a gelled acid is crucial in the success of this technique since it helps to divert the injected acid from the main flow regime into a relatively lower permeability zone by allowing the fluid to flow evenly and equally through the permeability zones. Since the main goal in these types of operations is to increase the permeability of the system, it is desirable that the acid is injected into the pay zone. However, sometimes the pay zone is difficult to reach due to a long height or various sublayers with different permeabilities[6,15]. So, in order to have a good distribution of the acid, engineers often use diverters, in this case gel diverters. The viscosity of the fluid changes by pH and temperature. Some materials would block the pores by “closing” or “bridging” near the well bore and using an impermeable seal or simply by producing a gel structure with high viscosity which blocks the permeability[4,6]. It has been reported in a study that silica nanoparticles were mixed in deionized water with a salt (magnesium chloride and electrolytes in order to modify the surface of the silica nanoparticles. They found that the reaction formed very stable gels and that is correlated to the concentration of the salt and pH by increasing the viscosity and therefore forming a gel[33].

Breaking Gelation

Once the fluid has been distributed properly through all the permeability zones of the system, the next step would be to break this gel to recover the fluid at some point which is not an easy task to achieve. It is still very complicate to break gelation at some planned time. In order to break the gel, it is necessary to decrease the viscosity. However, to decrease the viscosity, some changes in temperature or pH are needed. This is not desirable because after the injection of the fluid to the system it is not convenient to perform further injections. In the industry, once they propagate the fluid down the whole there is no way of increasing the temperature or pH by any natural means. Engineers are still finding a way to perform this task in an efficient manner[3,9,13].

Viscosity

The viscosity of the fluid is crucial in the efficiency of matrix acidizing techniques. An increase in the viscosity would lead to a higher-pressure loss and greater pumping power. The main parameters that would influence in the viscosity are particle size, diameter, concentration, shear rate, pressure and temperature. Fluids can be characterized as Newtonian or non-Newtonian based on the parameters discussed above. The viscosity of Newtonian fluids is only dependent on temperature which means that it doesn't matter how much they are forced to flow through a channel, viscosity will be the same[4,7]. Some examples of Newtonian fluids are organic solvents and water. For the most part, almost all fluids are non-Newtonian and their viscosity depend on shear rate. These fluids increase the viscosity with shear thickening as the shear rate increases and decrease the viscosity with shear thinning as the shear rate increases. These concepts are very important to fluid flow as it is well known that flow is strongly dependent on viscosity of fluids.

In matrix acidizing techniques a lot of different nanofluids systems have been observed to work effectively at some degree. Table 3 shows some of the typical nanofluids observed with their respective viscosities. Some of the most common fluids employed for acidizing applications during the last decade are iron oxide, aluminum oxide, silicon dioxide and zinc oxide. Some fluids have been reported to have increase in their viscosities due an increase in temperature for example iron oxide and aluminum oxide. However, some other fluids such as silicon dioxide it has not been reported to have an increase in viscosity with an increase in temperature[17].

Table 3. Typical nanofluids employed for matrix acidizing techniques.

Reference	Year	Material/Base Fluid	Fraction (vol% or wt%)	Particle Size (nm)	Additives	Viscosity Increase (%)
21	2011	Fe2O3/water	5-20 wt%	67	None	21%-36% at 10 °C 24%-49% at 30 °C 21%-36% at 50 °C 32%-72% at 70 °C
22	2010	Al2O3/water	0.33-5	43	None	236% at 5 vol %
23	2011	SiO2/oil	1.2-7	15	BAC	
24	2012	ZnO/EG	0.5-5.5	<100	None	

Particle size

The particle size is a very important factor in the viscosity of the system. It is known that the viscosity of a given nanofluid varies depending on the size of its particles. In a recent study it has been studied the particle size effect on the viscosity of alumina-water nanofluids. The results are shown in figures 1 and 2. They found that at a volume concentration of 4%, nanofluids of 36 and 47 nm size showed relatively the same viscosity but when the volume concentration of the fluid was increased then the fluid with the bigger nanoparticles (47 nm) had a higher viscosity than the other one[5]. Another study also supports this same idea, the viscosity of TiO_2 nanofluid suspended in water was studied at different particle sizes (95 and 145 nm). They found the same trend that as the particle size increases, the viscosity was found to be higher[4,8]. However, some contradictions to this point have been found in other studies. It has been reported that the viscosity of a SiO_2 nanofluid has been reduced with an increase in particle size. Also, other researcher was studying CuO and Al_2O_3 water nanofluids and ended up having similar results. They have explained that the trend found in this nanofluid behavior is because there is a higher interface resistance between the layers of the fluid due to a bigger surface area[3,4]. Even though there are many studies done in this topic and some of them contradict with each other it is concluded that viscosity is found to have a strong dependence on the size of the particle.

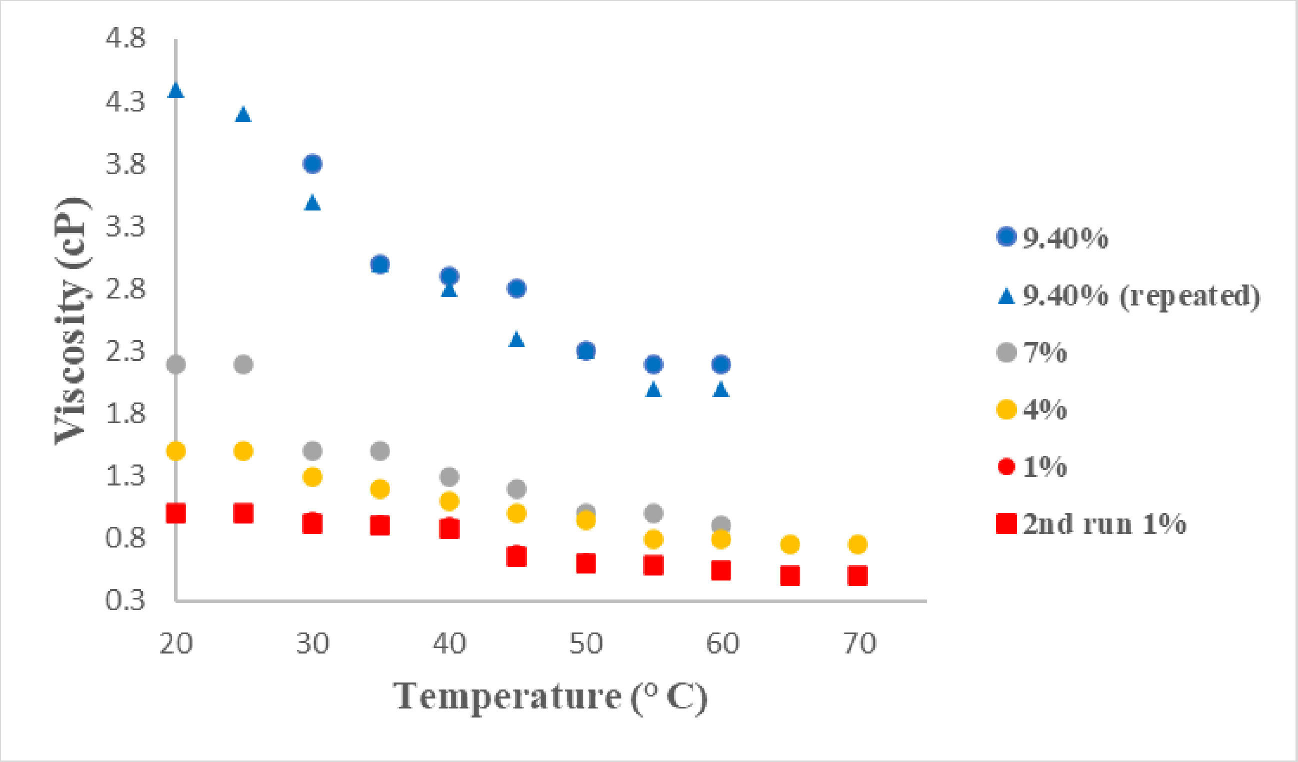


Figure 1. Viscosity data for water-Al2O3 – 47 nm fluid[2].

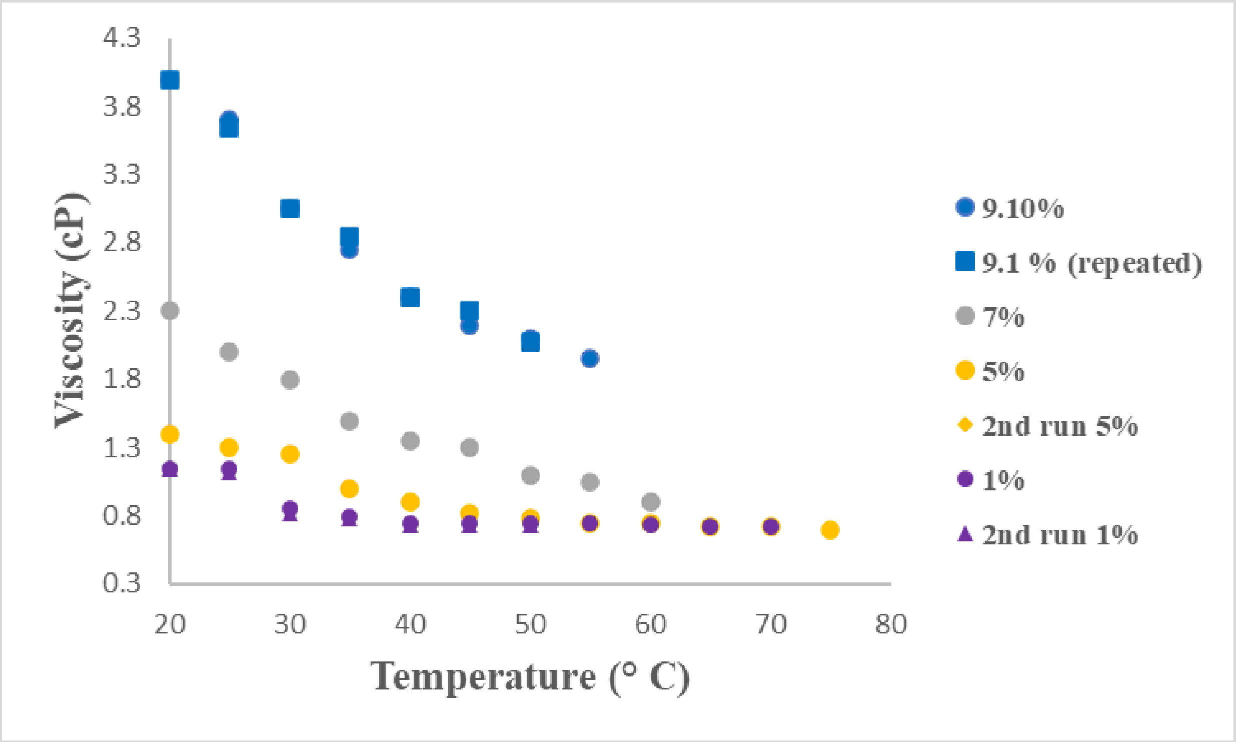


Figure 2. Viscosity for water-Al2O3 – 36 nm fluid[2].

Volume concentration

In general, the viscosity of nanofluids is found to increase when there is an increase in volume concentration. This is simply because viscosity is a property that measures the resistance to flow. An increase of the concentration of a fluid would increase the molecular weight and therefore thickening which would increase the viscosity as a result. However, this is not always the case as some studies have shown otherwise. For example, in a research study conducted by Hojjat, they were studying non-Newtonian fluids mainly showing shear-thinning behavior. They were doing analysis on power law indices (n) of nanofluids as a function of particle concentration at different temperatures and they found that the viscosity of Al_2O_3 and TiO_2 nanofluids generally increase when increasing the volume concentration but CuO nanofluids had a decrease in viscosity with an increase in volume concentration. They stated that this is possibly due to different interactions between nanoparticles and water molecules[3,9]. Many papers have been published studying how increasing or decreasing particle loading would affect the viscosity of a given nanofluid. In almost all the papers they found that the viscosity is greatly increased when the particle concentration is increased. In a study with alumina-water nanofluid reporting the viscosity change with change in volume they found that viscosity was increased with an increase in the volume concentration[12,18]. Also, other researchers reported a study on the Newtonian behavior of the same nanofluids between 1 and 4 % concentration and found the same results[23]. Another studies with TiO_2-water, Al_2O_3 and SiO_2-ethanol nanofluids were also investigated regarding this topic and the same results were found in both studies[7,13]. It is clear that the volume concentration has a great impact on the viscosity of the system. However, researchers have also reported that by the addition of more particles, the effect of viscosity could be detrimental to the heat transfer of the system and that the enhancement of viscosity with increase in volume concentration is found to be valid for most cases but not all of them. In another study they found that a CuO nanofluids was almost independent of the volume concentration[7,21,25].

Temperature

Another very important factor that influences drastically the viscosity is the temperature. It has been found a downward trend in the viscosity with an increase in temperature. This is because as the system gets hotter, the intermolecular attractions of the system weaken and therefore the viscosity decreases[4,6]. The overall reports in a summary indicate that in most of the cases a downward trend in viscosity when increasing the temperature is found. Some research studies done with SiO_2 and ZnO with a temperature range of 20-80 C and magnetic Fe_3O_4-water with a temperature range of 20-60 C support this idea and found the viscosity to be reduced after an increase of temperature[3,5]. However, there was one study in which they were working with Al_2O_3 and TiO_2 with a temperature range of 20-60 C in which they found no change in viscosity at all with the increase in temperature[13].

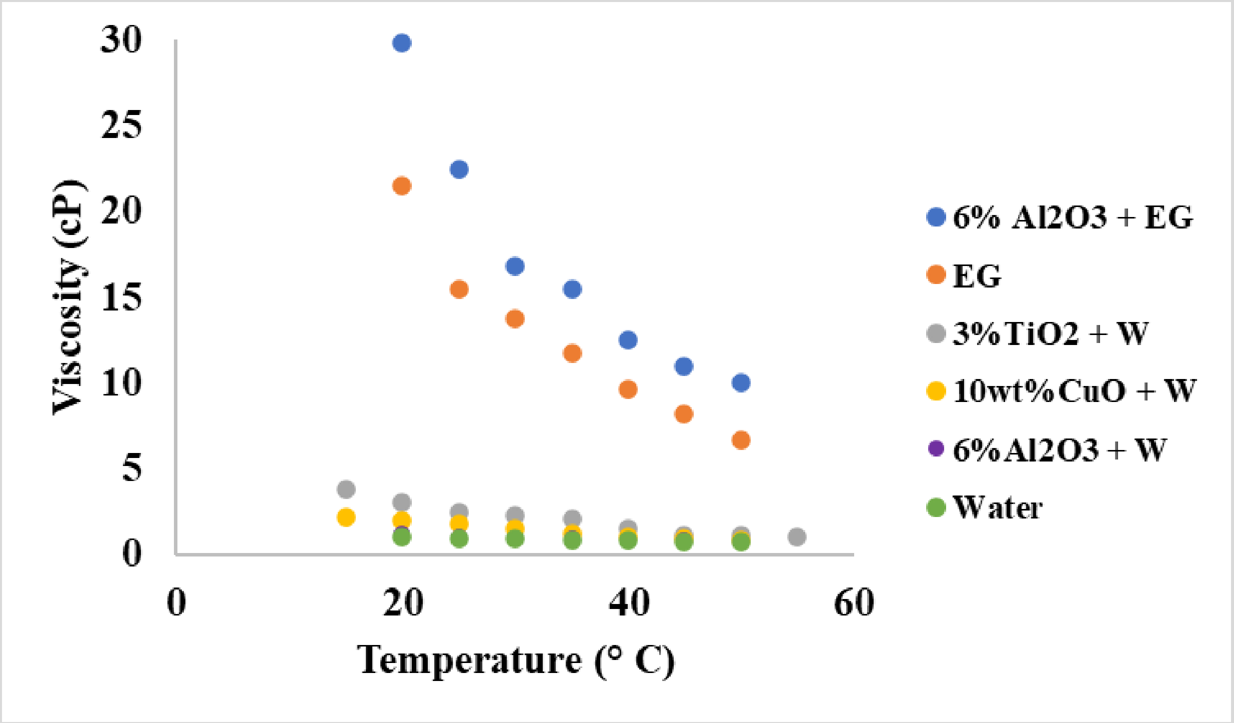


Figure 3. Viscosity decreases with increase in temperature for different nanofluids[5].

pH

Another very important factor that influence in the viscosity is the pH of the system. The viscosity of any system would change with a change in pH but it depends on the chemistry of the system. Some systems would change differently depending on their chemical nature. Several studies have found systems to work in these applications using the right pH for specific viscosities, but it strongly depends on the type of fluid they are working with. There has been a lot of research papers studying how pH influences the viscosity of nanofluids. Researchers have reported an optimal value of pH for a desired viscosity. In a paper examining the effect of pH on the stability of the system in which they used Sodium dodecyl benzenesulfonate (SDBS) as the surfactant and they were monitoring the pH using HCl and NaOH. The viscosity values at weight fraction 0.1, 0.2 and 0.4 % were found to be 0.826, 0.846, and 0.865 mPa/s for alumina and 0.82, 0.838 and 0.860 for copper with the same weight fraction and pH. They found that for alumina, a pH range of 7.5-8.9 and for copper a pH > 7.6 had a good dispersion and the viscosity remained stable for a long period of time[16]. Another study reported that for nanoparticles with small diameters (less than 20 nm) viscosity depends strongly on pH for silicon dioxide nanofluids. They found fluctuation between pH of 5-7 and a decrease in viscosity (unstable) for a pH below 5[6,15].

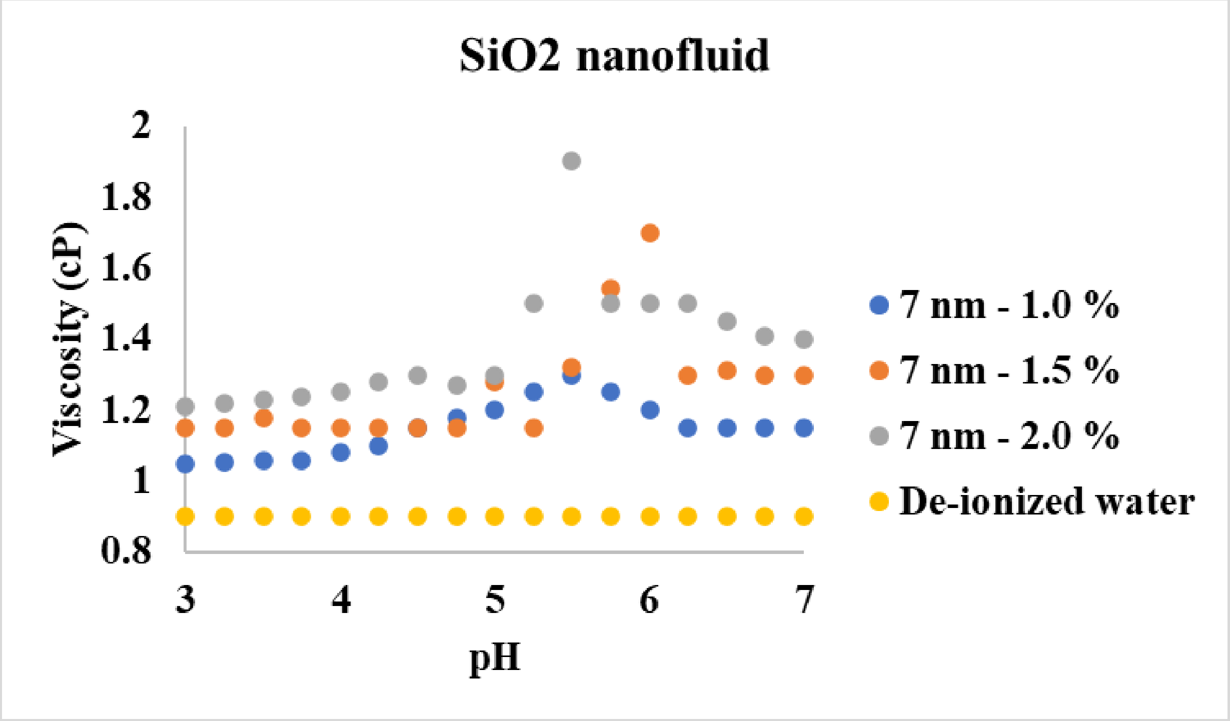


Figure 4. Viscosity of nanofluids and deionized water vs pH[5].

Shear rate

The shear rate is very useful at distinguishing from Newtonian and non-Newtonian fluids. This is because when there is an increase in the shear rate, the interactions between particles become weaker and they break at some point sometimes showing Newtonian behavior[13]. A recent investigation shows that CuO-water nanofluid and ethylene glycol nanofluid showed a Newtonian behavior whereas in another study with cobalt nanoparticles using the same base fluids they found the system to follow a non-Newtonian behavior[21]. Also, it has been observed in another study that Fe_2O_3-glycerol based nanofluid had a shear thinning behavior[2,6]. In another study, the viscosity of a system composed of FF-01 (15% w/w HCl) was analyzed versus shear rate using an Anton Paar rheometer at temperatures of 25, 40 and 60 C with different pressures of 100, 1000, 2000 and 3000 psi. It was found that the viscosity decreased with shear rate at rates higher than 300s-1 within the temperature range of 25-60 C. They stated that shear thinning is favorable during the injection of the fluid since high shear rates are typically experienced in the wellbore. Also, they found that small shear rates are experienced when the fluids reach the wormhole and when it generates fractures in the rock. They also found that increasing the pressure did not change the viscosity of the system and that FF-01 had a higher viscosity compared to conventional 15% HCl at different temperatures[5,12,26].

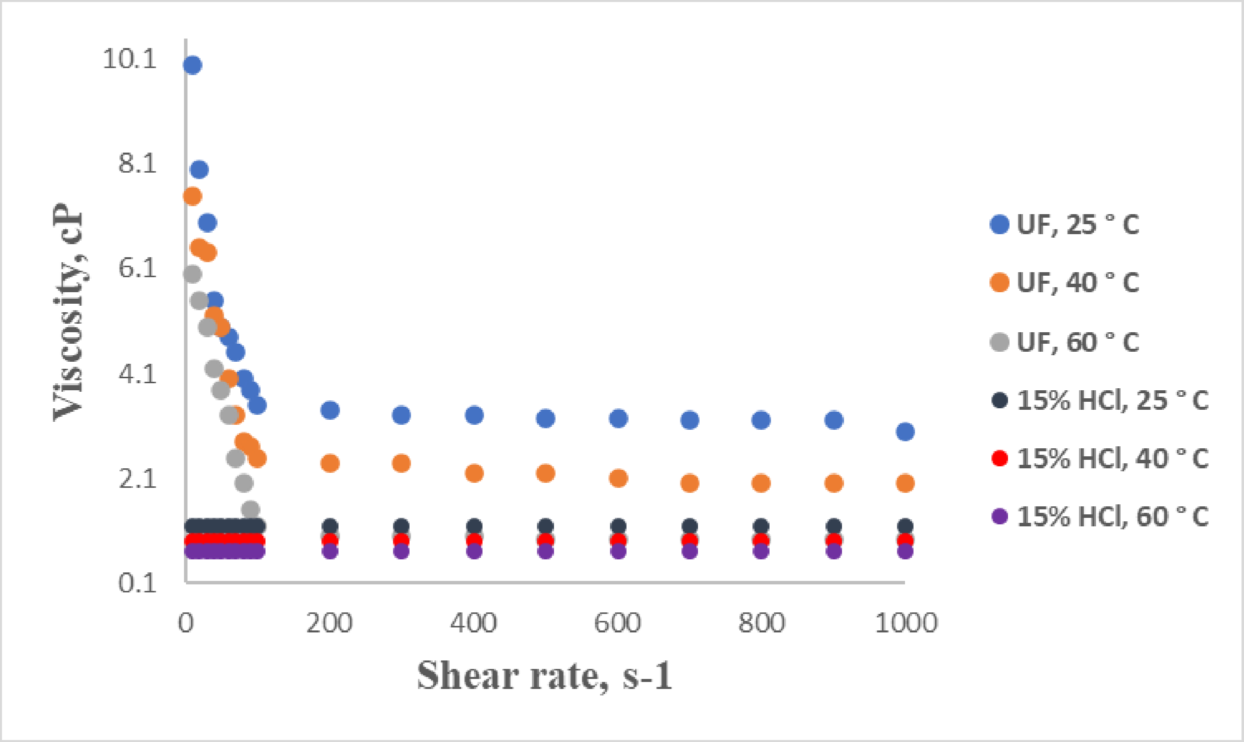


Figure 5. Viscosity vs shear rate for different nanofluids[12].

Enhancing Stability Procedures

Controlling the stability of the nanofluid is something crucial in order to achieve maximum effectiveness when performing treatment to the oil such as matrix acidizing. It has many advantages such as controlling the gelation process or just the wide number of different scenarios in which this treatment could be employed in such an effective manner. There are a few processes by which someone could enhance the stability of the nanofluids, the most common approaches are: adding a surfactant, using a surface modification technique and having a pH control of nanofluids[1,3,15].

Addition of Surfactants

This process is also known as dispersant, is a very effective way of increasing the stability of the nanofluid by preventing the nanoparticles to agglomerate with the nanofluid. It is an economic and simple chemical method which enhances the immersion of the nanoparticles by reducing the surface tension of the system. Surfactants are a long chain of hydrocarbons which consist of a hydrophobic and hydrophilic tails that increase the attraction between the fluid and the nanoparticles in the system. The surfactants are divided into four main classes: ionic surfactants, nonionic surfactants, cationic surfactants and amphoteric surfactants. Selecting the right surfactant to use is something crucial in order to succeed in the process, this depends on the type of nanofluid someone is working with, if the fluid is polar then a water soluble surfactant should be employed, if the fluid is nonpolar then an oil based surfactant should be used rather. However, one of the main disadvantages of using surfactants is that they are very sensitive to high temperatures. This is because the increase in temperature causes more collisions and the bonds produced by the surfactant and the fluid become damaged. Also, if too much surfactant is added to the fluid it alters the thermophysical properties creating a problem by increasing the viscosity and reducing thermal conductivity[3,5].

Surface Modification Technique

Another alternative instead of using surfactants is by employing a surface modification technique. This method has a long-term stability of the nanofluid, the surface of the nanoparticles is modified via functionalization. In general, for an optimization in a higher breaking strength, the scratch resistance and even a mechanical property like Young’s modulus, there must be a chemical alteration in the surface of the nanofluid in order to strengthen interface bonding[3,12,24]. These functionalized nanoparticles are introduced in the fluid in order to stabilize it. In this method, functional organic groups are commonly used since they attach easily to the surface atoms which enables the self-organization of the nanoparticles to occur and therefore avoiding agglomeration. The functional groups can be introduced to the fluid by two approaches. The first one is by introducing the ligands in one step which requires the functional organic compounds. The second approach is by producing a reaction between the functional organic compounds and coupling a group with the fluid. One of the biggest challenges when using this technique is that the process of the incorporation of any ligand molecules onto the nanofluid employed is very complicated to keep the colloidal stability of the system during the functionalization process. This technique has been widely studied and it has been found that is very dependent on the nature of the nanoparticle composition [13].

pH Control

One important factor to consider when enhancing the stability of the nanofluid system is that manipulating the pH of the system is another way of changing the nature of the surface of the nanoparticles and can bring some advantages to the table such as manipulating the stability by increasing or decreasing the pH value. This happens because some electrokinetic properties are strongly related to the stability of the fluid.

When the zeta potential is increased or decreased by changing the pH the nanosystem becomes more stable because there higher repulsive forces between the nanoparticles. When developing the nanofluid system someone can simply alter the pH by adding enough acid or base depending if they need to increase or decrease pH[4,12,18].

CHAPTER II

MATERIALS AND METHODS

Silicon dioxide nanopowder

Silicon dioxide nanopowder, 10-20 nm particle size (BET) was bought from Sigma-Aldrich and it was utilized for all of the experiments in this project. It has a pH from 3.7 – 4.7, density of 2.2 – 2.6 g/mL.

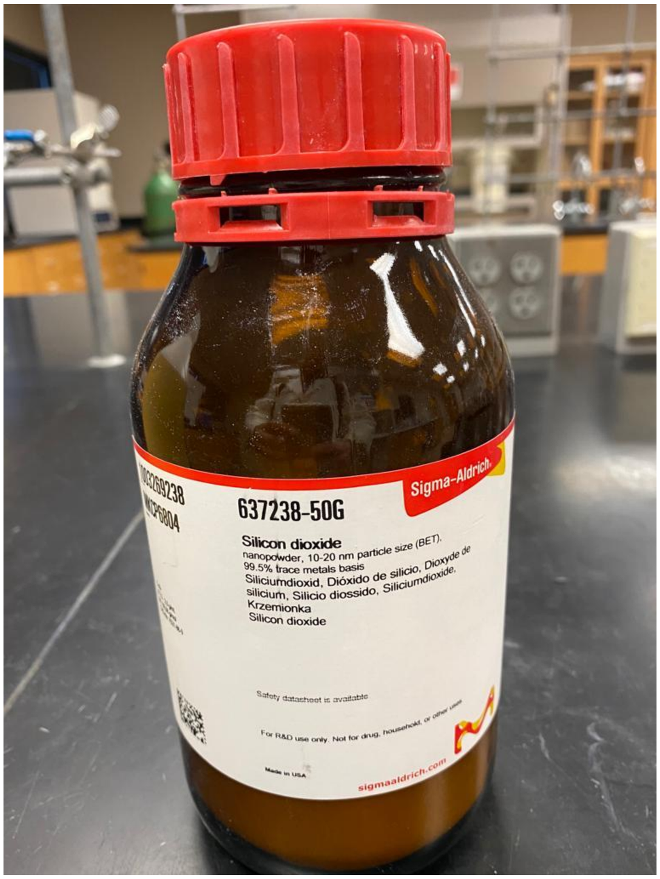


Figure 6. Silicon dioxide nanopowder.

Indiana limestone

Indiana limestone was utilized for these experiments.

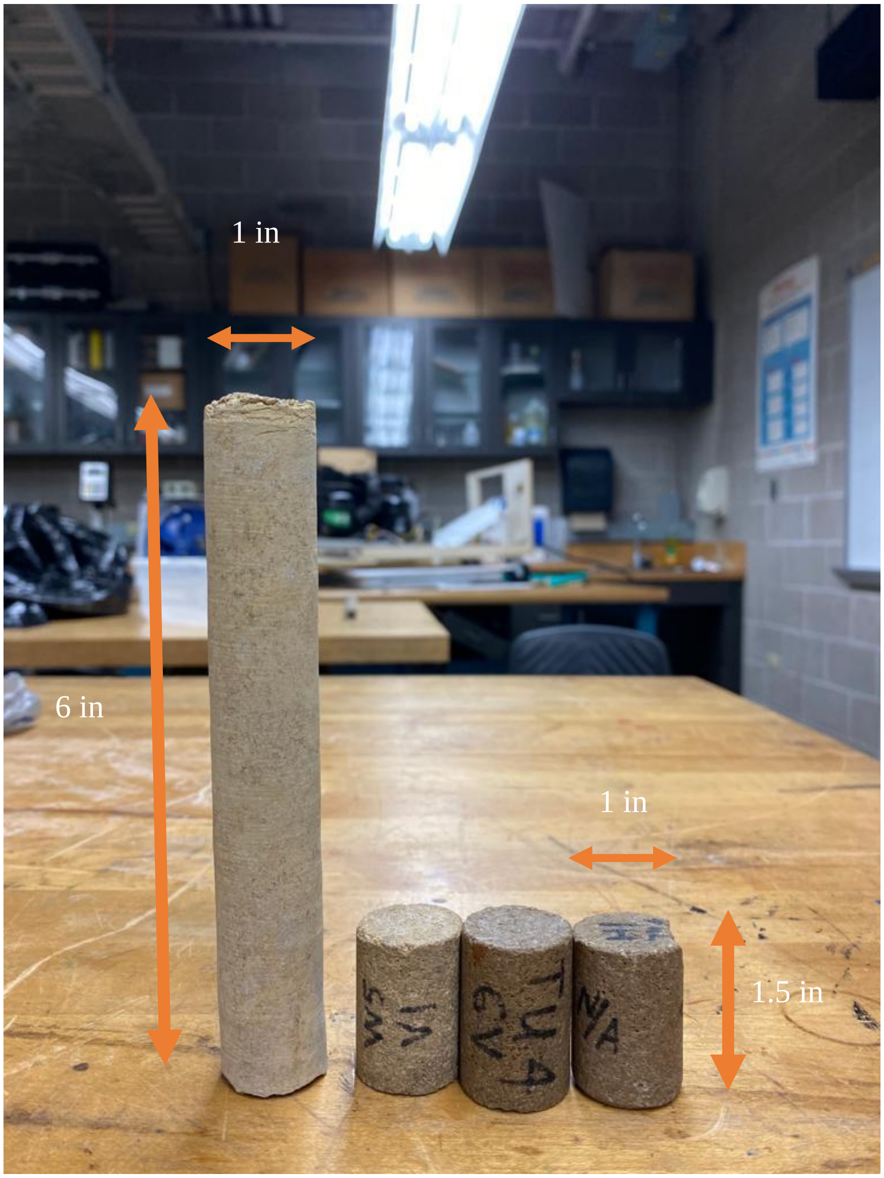


Figure 7. Indiana limestone.

Bioterge AS-40 surfactant

Bioterge AS-40 surfactant was bought from Voyageur soap and candle corporation and it was utilized for these experiments. It has a pH of 11.7, density of 1.05 g/mL and viscosity of less than 500 cP.

Figure 8. Surfactant Bioterge AS-40.

15% Hydrochloric acid

Hydrochloric acid was utilized for all the coreflood experiments. It has a pH of less than 1, density of 1.07 g/mL and viscosity of 0.015 cP.

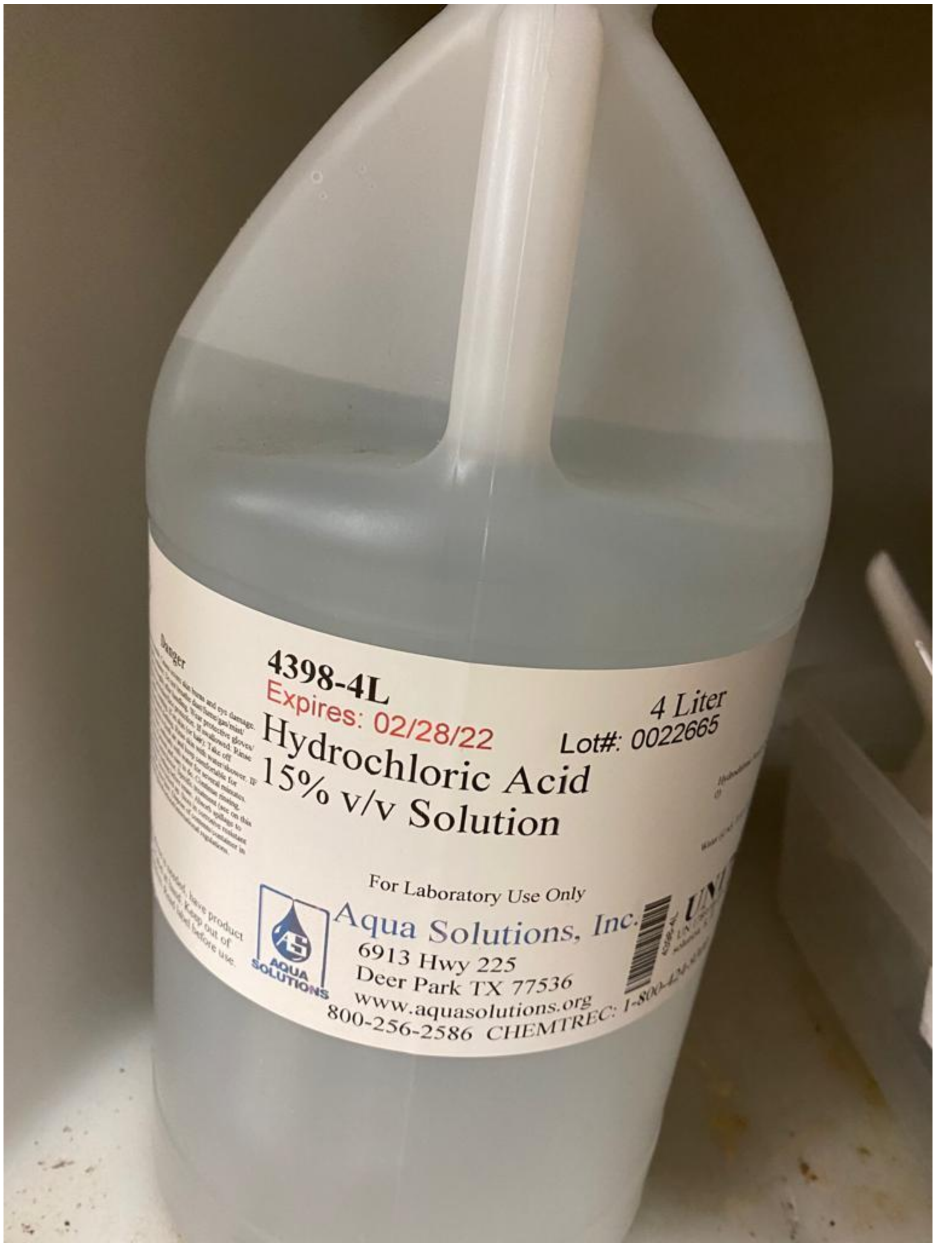


Figure 9. 15% Hydrochloric acid solution.

Sonicator

Sonicator 5800 from Branson was utilized to perform reactions in these experiments. The samples were placed in the sonicator to mix for 20 minutes with a frequency of 40 kHz. The operating temperature range is from 5 °C to 40 °C (41 °F to 104 °F), temperature readout accuracy is found to be ± 3 °C (± 5.4 °F). It has a ground leakage current of less than 0.50 ma.

Figure 10. Sonicator.

Rheometer

Rheometer DV – III ULTRA from Brookfield was utilized to measure the viscosities of the experimets. All of the samples were taken to the rheometer in order to measure the viscosity after each sample was made and every couple of hours after. It has an accuracy of ± 1.0% of full scale range for a specific spindle running at a specific speed. It has a temperature accuracy of ± 1.0°C from -100°C to 150°C. The rheometer was found to have a viscosity range of 1 to 2 million cP according to the manual.

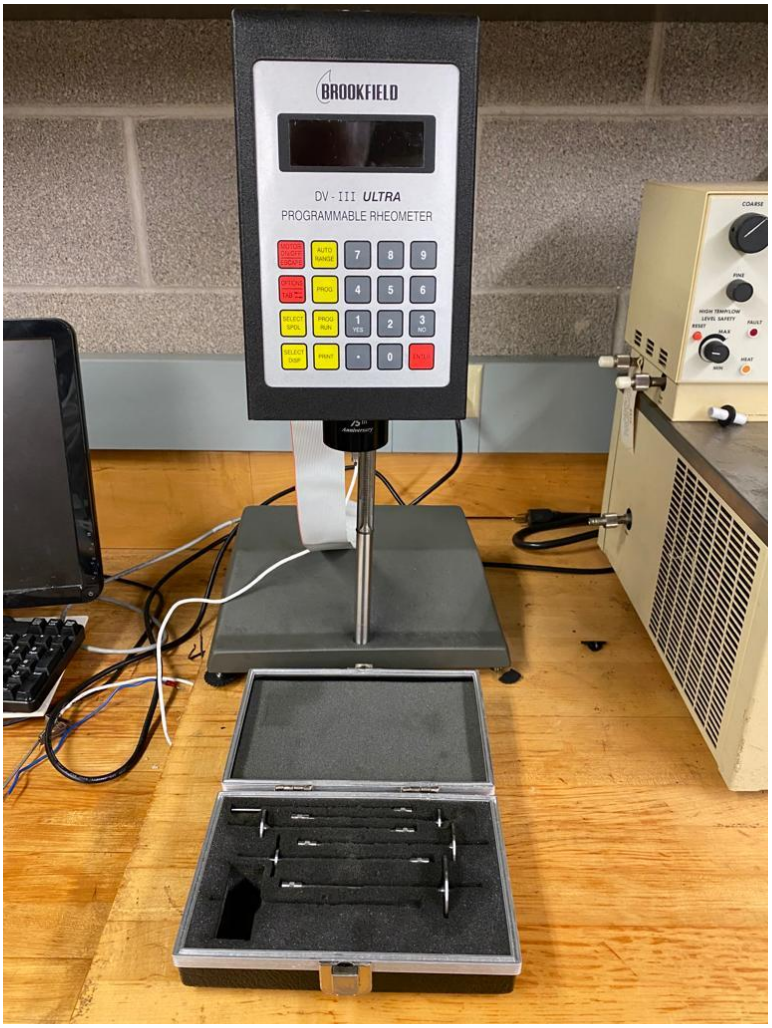


Figure 11. Rheometer.

Balance

A weighing balance was utilized to prepare samples of the fluid. It has an accuracy of ± 1 division.

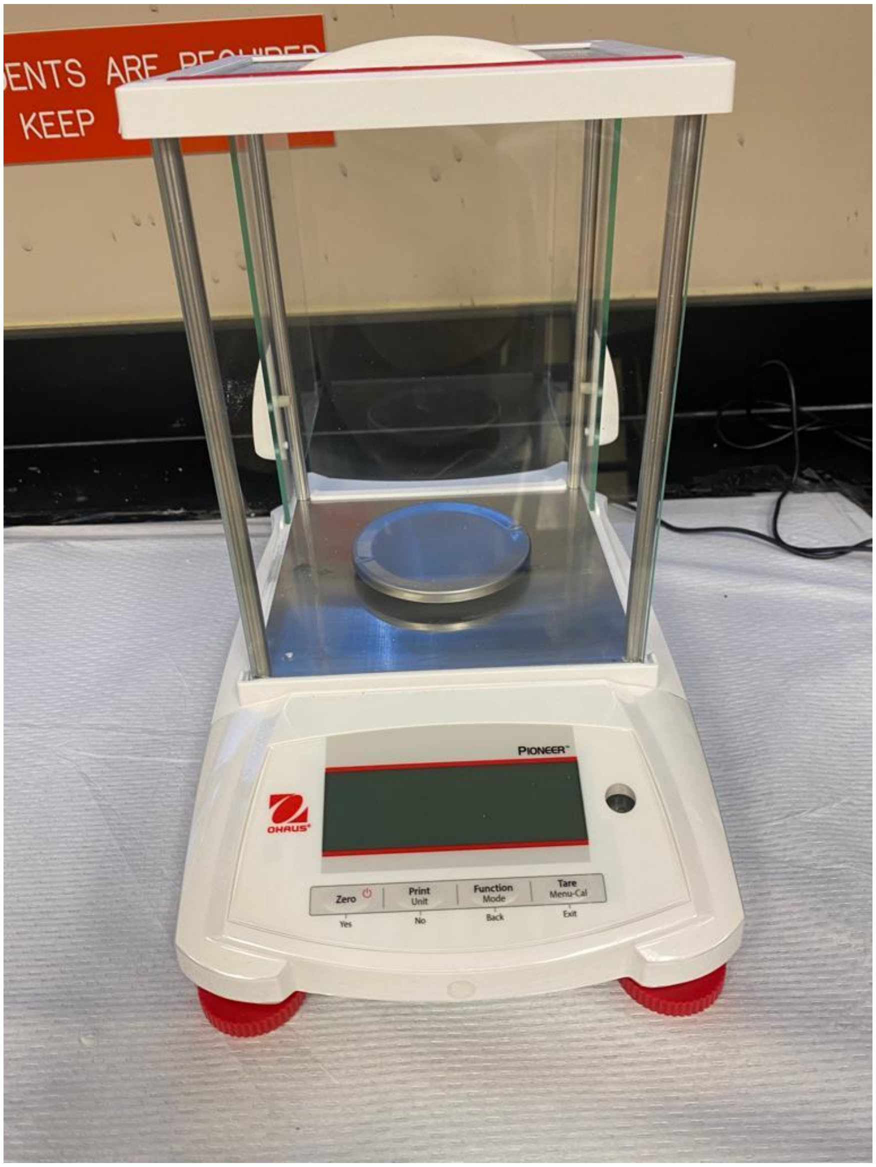


Figure 12. Balance.

Coreflood apparatus

A coreflood apparatus built in the lab was utilized to perform injections at high pressures on the samples. This coreflood set up consists of two electrical pumps, one manual pump, two accumulators, stainless steel lines, core holder, pressure gauges, three diffusers and a nitrogen tank.

Figure 13. Coreflood apparatus set up.

pH meter

A pH meter was utilized to measure the changes in pH of the samples. Each of the samples was adjusted in pH after the reactions were complete to further investigate the effects of the pH in gelation. It has an accuracy of ± 0.1.

Figure 14. pH meter.

Propagation of nanofluid into Indiana limestone cores

Twenty-five mL samples are going to be prepared with hydrophobic silica nanoparticles and surfactant Bioterge AS-40 with a total nanoparticle concentration of 2.5 vol % with 97.5 vol% deionized water and 3 wt% NaCl. Some of the samples are going to be made without surfactant and some without salt. The samples are going to be mixed with vortex and used a horn sonicator with 25% amplitude for 20 minutes. The pH of the sample is then going to be adjusted using 10 vol% NaOH and 10 vol% HCl solutions. Independent samples are going to be prepared for each pH value tested to avoid dilution in the nanoparticle gel via addition of further NaOH or HCl solution. These experiments are going to be executed in triplicates to get more accurate results. In this set of experiments, the pH range was adjusted to about 1.5, 3, 7, 11 and 12.5. Experiments in table 6 consisted of 2.5 vol% silica nanoparticles without surfactant and without salt. Experiments in table 7 included 2.5 vol% silica nanoparticles with surfactant and without salt. Experiments in table 8 included 2.5 vol% silica nanoparticles with salt and without surfactant. And lastly, experiments in table 9 consisted of 2.5 vol% silica nanoparticles with surfactant and salt. The goal here is to find the best parameters for the fluid that make it more viscous and therefore producing a gel. The experiments are going to be checked every couple of hours to analyze the process. The gelation region is expected to be found somewhere between pH 5 to 11.6.

Table 4. Experiment parameters.

Sample	pH	Vol % of silica nanoparticles	Amount of Bioterge AS-40 in mL	NaCl in grams
1	1.45	2.5	5	1.25
2	1.39			
3	1.42			
4	2.99			
5	2.94			
6	2.93			
7	6.92			
8	7.1			
9	7.08			
10	11.25			
11	11.22			
12	11.18			
13	12.48			
14	12.42			
15	12.46			

The calculations for the reactions are represented as follows.

Amount of reactants used.

- 1.25 g of Silica.
- 1.25 g of NaCl.
- 5 mL of surfactant Bioterge AS-40.
- 22.7 mL of deionized water.

Since the density of the surfactant is 1.06 g/mL, the amount of surfactant in grams can be calculated as follows:

$$1.06 = \frac{g}{5}$$

$$grams\ of\ surfactant = 5.3$$

The amount of water used in grams can also be calculated the same way, the density of water is found to be 1 g/mL.

$$1 = \frac{g}{22.7}$$

$$grams\ of\ water = 22.7$$

The weight % of salt used in the experiments can be calculated with the following equation:

$$weight\ \% = \frac{mass\ of\ solute}{mass\ of\ solution}$$

$$weight\ \%\ of\ NaCl = \frac{1.25\ g}{30.5\ g}\ x\ 100 = 4\%$$

Then, the weight % of surfactant Bioterge AS-40 can be calculated the same way.

$$weight\ \%\ of\ Bioterge\ AS - 40 = \frac{5.3\ g}{30.5\ g} x\ 100 = 17\%$$

This study is going to help in finding the best pH value at which the fluid creates a gel so that when the coreflood experiments are performed the gel would form during injection. The next step would be to test different vol % of our fluids (1, 1.25, 1.5, 1.75) and then with some crushed Indiana limestone (5 g) added in the vials to understand what the effect of having a different vol % of the fluid is in creating a gel and what is the effect that the added Indiana limestone has in forming the gel. It is expected that the addition of the Indiana limestone would enhance the gelation due to its strong affinity to water molecules. In these set of experiments, the effect that vol % has in the gelation process is going to be analyzed. Now, to analyze the effect of the added Indiana limestone to the gelation process, a different set of experiments analyzing 1 vol % of the silica nanoparticles with 5 grams of crushed Indiana limestone is going to be performed. This is represented in tables 13, 14 and 15.

The last set of experiments was performed as represented in table 15 and 16. Here, a set of 2.5 vol% of silica nanoparticles with surfactant is compared to a set of 2.5 vol% of silica nanoparticles without surfactant. Both experiments consisted of salt and a 15 wt% HCl was added with a small sample of Indiana limestone to observe how the pH changes and if a gel is formed. The third sample was made of only pure 15% HCl used as a baseline and reacting with a sample of Indiana limestone to compare the reactions between the three.

Coreflood experiments for acidizing

In this set of experiments, the goal was to analyze the propagation of the fluid through the rock. Test A consisted of only acid and it would be used as a baseline case experiment, test B consisted of 2.5 vol% of silica nanoparticles in deionized water, 3wt% NaCl and a slightly basic pH of 7.4. This is represented in table 17. This nanoparticle concentration and pH were found to be the best among the first study, which is represented in table 7.

After the results were analyzed, a graph plotting the change in pressure from the transducers versus the time was made. When the change in pressure approached 0 it meant that the fluid has successfully propagated the rock.

CHAPTER III

RESULTS AND DISCUSSION

Rheometer calibration errors

The accuracy of the rheometer was tested by reading the viscosities of two common fluid with known viscosities to figure out how miss calibrated the rheometer was. This is represented in table 5. Olive oil has a known viscosity of 40 cP and the recorded viscosity was found to be 60 cP. Hydraulic oil has a known viscosity of 35 cP and the recorded viscosity was found to be 60 cP as well. During the experiments, spindle number 6 was selected for the viscosity measurements because it was found to be the most accurate. Spindle number 6 was utilized throughout all the experiments. When using spindle number 6, the viscosity increases in intervals of 20 cP. The rheometer is a little bit off (by 20 cP) when taking measurements of olive oil and hydraulic oil with spindle number 6.

Table 5. Rheometer accuracy tests.

Sample	Expected Viscosity (cP)	Recorded Viscosity (cP)
Olive Oil	40	60
Hydraulic Oil	35	60

Propagation of nanofluid into Indiana limestone cores

The first set of experiments are represented in tables 6, 7, 8 and 9 and were performed in triplicates to come up with results more consistent. In this set of experiments, the pH range was adjusted to about 1.5, 3, 7, 11 and 12.5. As it can be seen in figures 20, 21 and 22, gelation at a very acidic and very basic pH the gel is hard to form and that close to neutral pH the gel is easier to be formed. It was also found that the best experiments in which gelation was seen more obvious are the ones that involve a pH neutral to basic with a range from 7-11. In this research paper, gelation refers when the fluid starts to change from a liquid state to a more solid state. It is when the fluid becomes thicker and slightly sticky (gel instead of liquid). It was observed that the fluid containing only silica nanoparticles was the one with more difficulties in forming the gel. But it was very similar to the one with silica, surfactant and without salt. On the other hand, the fluid containing silica, surfactant and salt was the one that formed a gel easier in the least amount of time and with the higher values of viscosities. Also, the fluid containing silica, and salt without surfactant showed very similar results making these two last fluids the best options for injection in the coreflood apparatus. Even though the fluid that contains the surfactant showed slightly higher viscosity values for some samples, it is negligible since viscosities are almost the same.

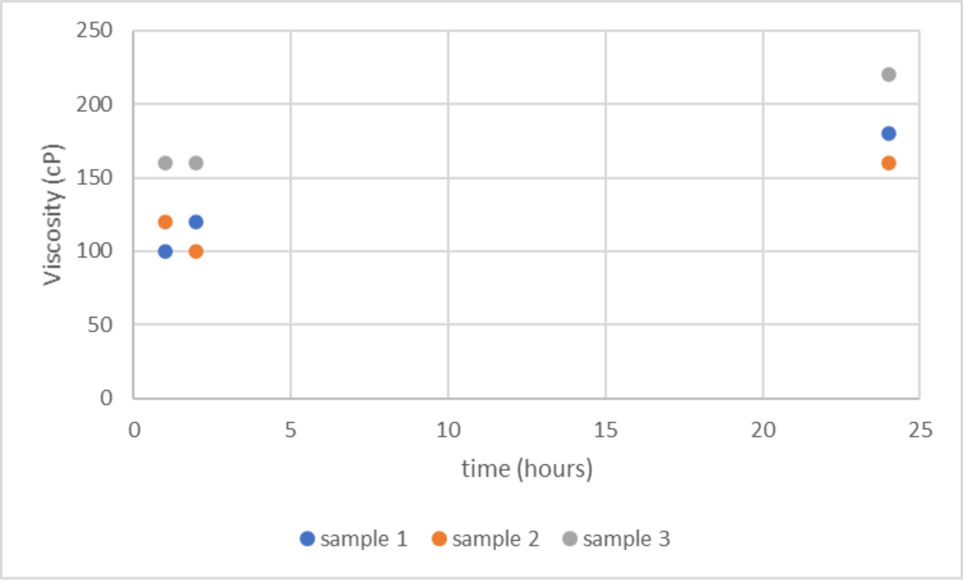


Figure 15. Consistency of experiments.

In this graph, the consistency and repeatability of the experiments (triplicates) was analyzed. It can be seen that the viscosity values for the experiments at a very acidic pH are very close.

Table 6. Triplicate of 2.5 vol% silica nanoparticles without NaCl and without surfactant.

Type	Sample	pH	Vol % of silica nanoparticles	Viscosity (cP) after 1 hour	Viscosity (cP) after 2 hours	Viscosity (cP) after 24 hours	Gelation after 1 hour	Gelation after 2 hours	Gelation after 1 day
Very acidic	1	1.42	2.5	100	120	180	No	No	Yes
	2	1.43		120	100	160	No	No	Yes
	3	1.48		160	160	220	No	Yes	Yes
Acidic	4	2.9		120	140	260	No	Yes	Yes
	5	2.93		120	140	280	No	Yes	Yes
	6	2.84		120	140	280	Yes	Yes	Yes
Neutral	7	6.9		140	180	320	Yes	Yes	Yes
	8	6.93		80	120	320	Yes	Yes	Yes
	9	7.1		140	160	340	Yes	Yes	Yes
Basic	10	11.3		80	100	280	No	Yes	Yes
	11	11.15		100	120	300	No	Yes	Yes
	12	11.16		120	160	280	No	Yes	Yes
Very basic	13	12.4		100	120	240	No	Yes	Yes
	14	12.21		80	100	260	No	No	Yes
	15	12.34		180	220	260	No	No	Yes

It can be seen in table 6 that all the samples formed a gel after 1 day. Most of the samples formed the gel after 2 hours, and only a few could form a gel after 1 hour. The gelation state was determined by visual observation. It was found that the nanofluid tends to form a gel with time, as the fluid gets more viscous. However, in very few of the cases it was seen otherwise. For example, sample 15 did not form a gel after 2 hours even though it was found to have a viscosity value of 220 cP. Whereas sample 3 did form a gel with a viscosity of 160 cP. More than likely this is due to a human error when performing viscosity measurements.

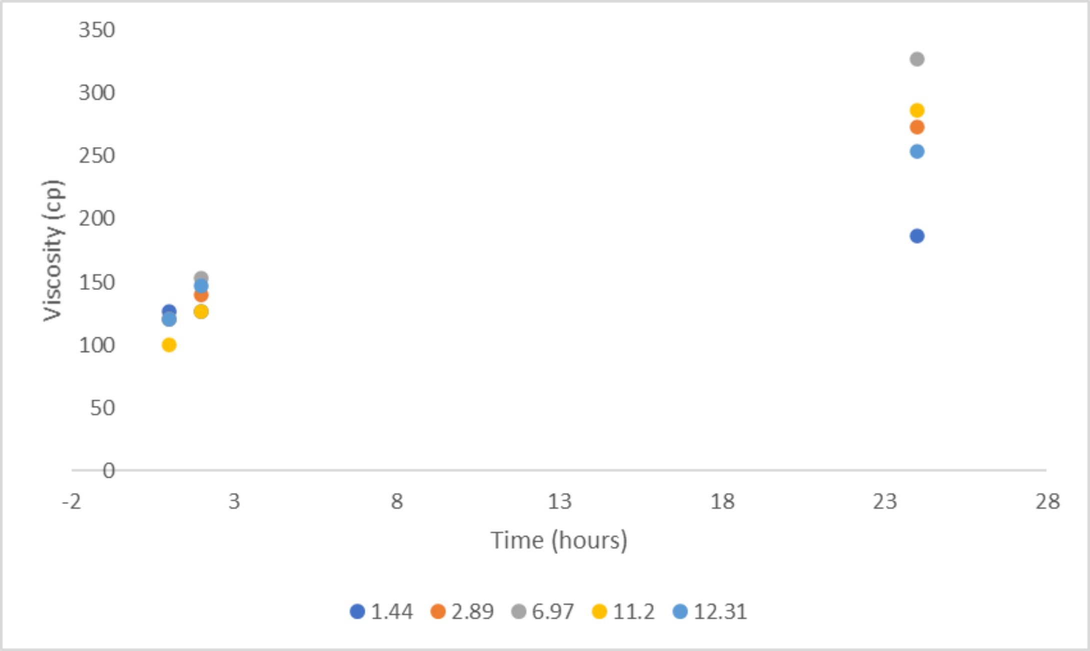


Figure 16. Viscosity vs time graph triplicates from table 4.

Table 7. Triplicate of 2.5 vol% silica nanoparticles with Bioterge AS-40 and without NaCl.

Type	Sample	pH	Vol % of silica nanoparticles	Amount of Bioterge AS-40 in mL	Viscosity (cP) after 1 hour	Viscosity (cP) after 2 hours	Viscosity (cP) after 24 hours	Gelation after 1 hour	Gelation after 2 hours	Gelation after 1 day
Very acidic	1	1.71	2.5	5	200	180	280	No	No	Yes
	2	1.62		5	180	220	300	No	Yes	Yes
	3	1.66		5	160	200	280	Yes	Yes	Yes
Acidic	4	2.91		5	140	160	280	No	Yes	Yes
	5	2.98		5	200	200	300	Yes	Yes	Yes
	6	2.97		5	180	180	240	Yes	Yes	Yes
Neutral	7	6.91		5	200	220	340	Yes	Yes	Yes
	8	6.92		5	180	220	340	No	Yes	Yes
	9	6.96		5	180	200	320	Yes	Yes	Yes
Basic	10	11.16		5	180	200	320	Yes	Yes	Yes
	11	11.23		5	180	240	340	No	Yes	Yes
	12	11.14		5	220	240	300	No	Yes	Yes
Very basic	13	12.49		5	160	160	240	No	Yes	Yes
	14	12.47		5	160	180	260	No	No	Yes
	15	12.51		5	140	160	260	No	No	Yes

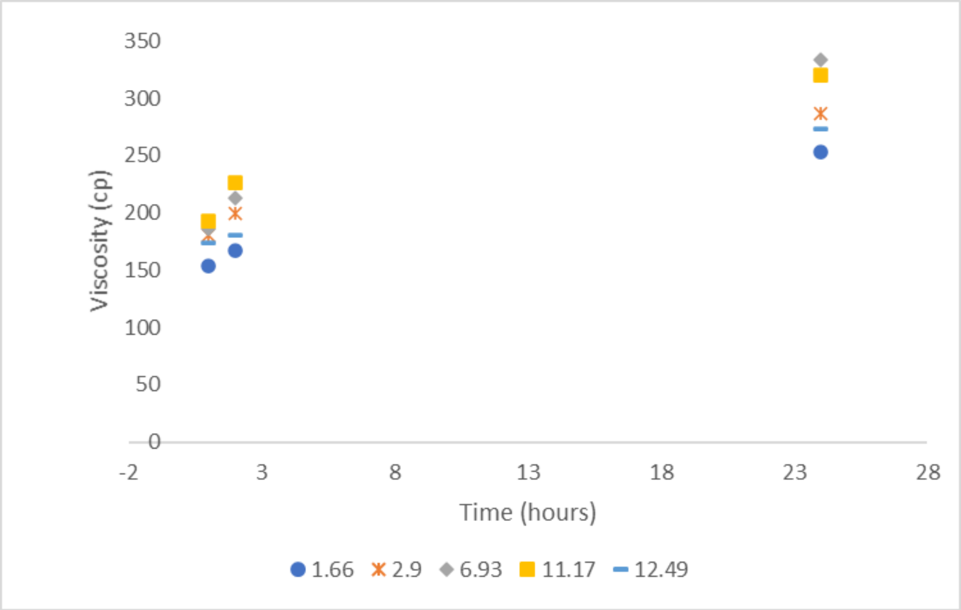


Figure 17. Viscosity vs time graph triplicates from table 5.

Table 8. Triplicate of 2.5 vol% silica nanoparticles without Bioterge AS-40 and with NaCl.

Type	Sample	pH	Vol % of silica nanoparticles	NaCl in grams	Viscosity (cP) after 1 hour	Viscosity (cP) after 2 hours	Viscosity (cP) after 24 hours	Gelation after 1 hour	Gelation after 2 hours	Gelation after 1 day
Very acidic	1	1.42	2.5	1.25	80	120	140	No	No	No
	2	1.38		1.25	100	100	120	No	No	Yes
	3	1.41		1.25	60	80	120	No	No	No
Acidic	4	2.95		1.25	160	200	280	No	No	No
	5	2.94		1.25	240	280	320	No	No	Yes
	6	2.98		1.25	260	280	340	No	No	Yes
Neutral	7	7.14		1.25	240	320	400	Yes	Yes	Yes
	8	7.06		1.25	260	300	340	Yes	Yes	Yes
	9	7.12		1.25	280	320	400	Yes	Yes	Yes
Basic	10	11.15		1.25	240	280	360	Yes	Yes	Yes
	11	11.24		1.25	300	360	380	Yes	Yes	Yes
	12	11.28		1.25	300	340	400	Yes	Yes	Yes
Very basic	13	12.35		1.25	100	120	140	Yes	Yes	Yes
	14	12.31		1.25	80	100	180	No	No	Yes
	15	12.36		1.25	100	120	140	No	Yes	Yes

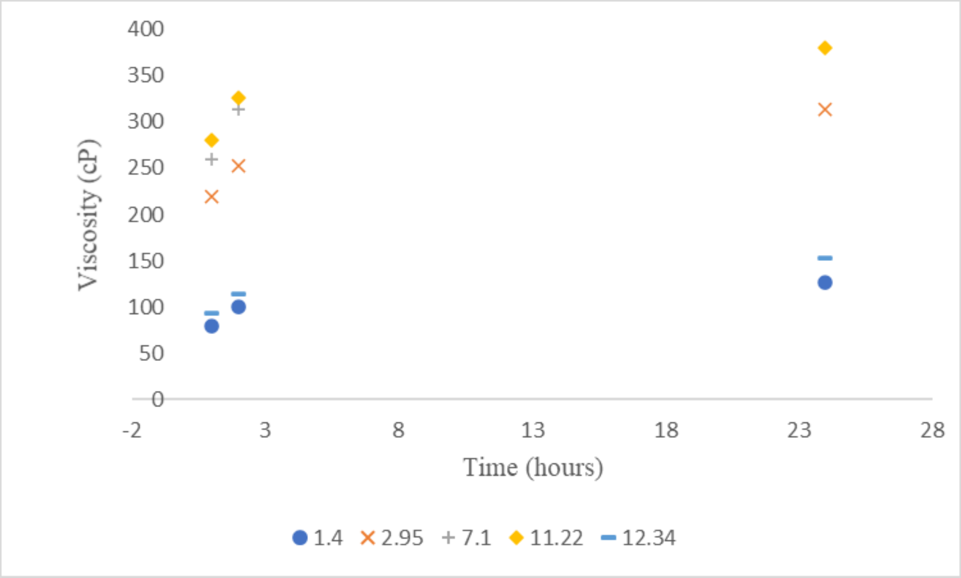


Figure 18. Viscosity vs time graph triplicates from table 6.

Table 9. Triplicate of 2.5 vol% silica nanoparticles with Bioterge AS-40 and NaCl.

Type	Sample	pH	Vol % of silica nanoparticles	Amount of Bioterge AS-40 in mL	NaCl in grams	Viscosity (cP) after 1 hour	Viscosity (cP) after 2 hours	Viscosity (cP) after 24 hours	Gelation after 1 hour	Gelation after 2 hours	Gelation after 1 day
Very acidic	1	1.45	2.5	5	1.25	100	120	160	No	No	No
	2	1.39		5	1.25	80	100	140	No	No	Yes
	3	1.42		5	1.25	100	100	120	No	No	No
Acidic	4	2.99		5	1.25	180	200	300	No	No	No
	5	2.94		5	1.25	260	280	340	No	No	Yes
	6	2.93		5	1.25	240	260	360	No	No	Yes
Neutral	7	6.92		5	1.25	260	360	420	Yes	Yes	Yes
	8	7.1		5	1.25	280	340	380	Yes	Yes	Yes
	9	7.08		5	1.25	300	360	420	Yes	Yes	Yes
Basic	10	11.25		5	1.25	240	320	380	Yes	Yes	Yes
	11	11.22		5	1.25	320	340	400	Yes	Yes	Yes
	12	11.18		5	1.25	280	340	400	Yes	Yes	Yes
Very basic	13	12.48		5	1.25	120	140	160	Yes	Yes	Yes
	14	12.42		5	1.25	100	100	200	No	No	Yes
	15	12.46		5	1.25	120	100	120	No	Yes	Yes

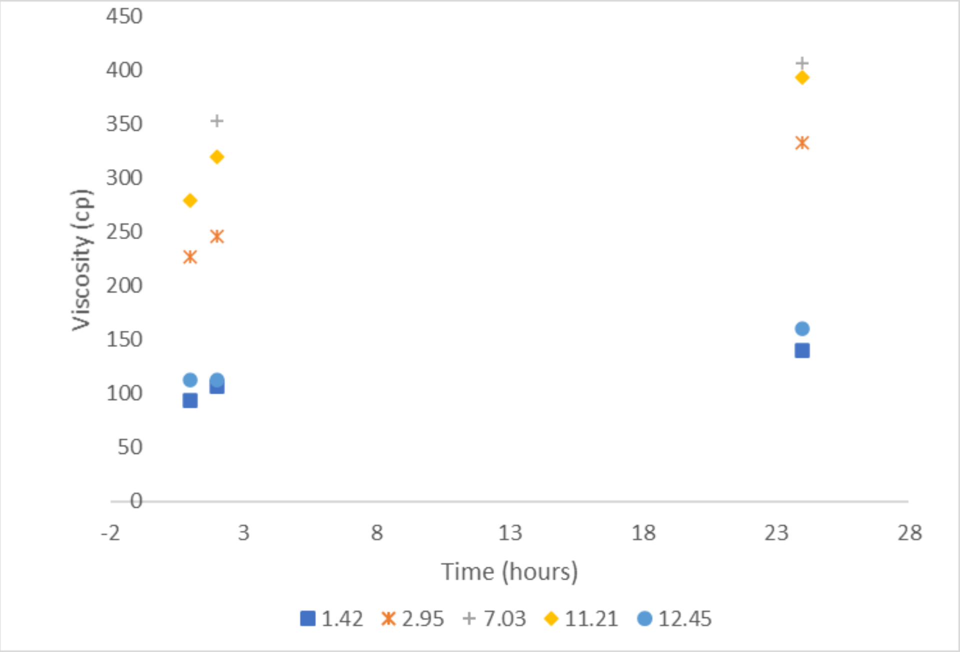


Figure 19. Viscosity vs time graph triplicates from table 7.

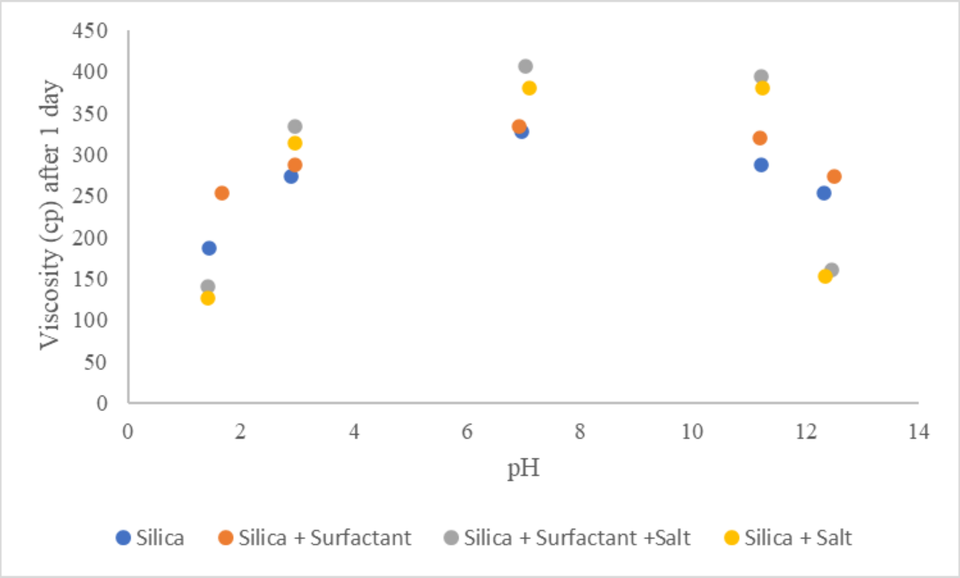


Figure 20. Viscosities vs pH graph for all triplicates.

Analyzing the graphs collected in these sets of experiments (figures 16-20), it can be concluded that the fluid containing silica, surfactant and salt is the fluid with the highest viscosity at a pH of 7 (420 cP) The fluid containing silica and salt only is the second highest viscosity at a pH of 7 (400 cP). These two fluids are very similar, even though the fluid containing silica, salt and surfactant has slightly higher viscosities, it can be concluded that both fluids are the best to inject in the coreflood experiments. The fluid containing silica and surfactant is very similar to the fluid containing only silica. Both had the highest viscosity to be found at a pH of 7 (340 cP). It can be concluded that when using surfactant, the viscosities increased slightly among the different pH range but it was very similar than the fluid without surfactant. On the other hand, analyzing the fluid containing salt and the fluid without salt, it can be concluded that the use of salt has a greater influence in the increase of the viscosity compared to the use of surfactant. Salts, specifically sodium chloride, are common accelerators for inducing gelling in silica. As it has been mentioned earlier, the pH affects viscosity depending on the chemical nature of the fluid only. The fluid developed in this research study seems to increase with a pH neutral to basic (7-10). The highest value for viscosity was 420 cP and it was found at a pH of 7.

Figure 21. Triplicates from table 4 and 5.

Figure 22. Sample 7 from table 7.

Figure 23. Sample 9 from table 6.

Figure 24. Sample 3 from table 5.

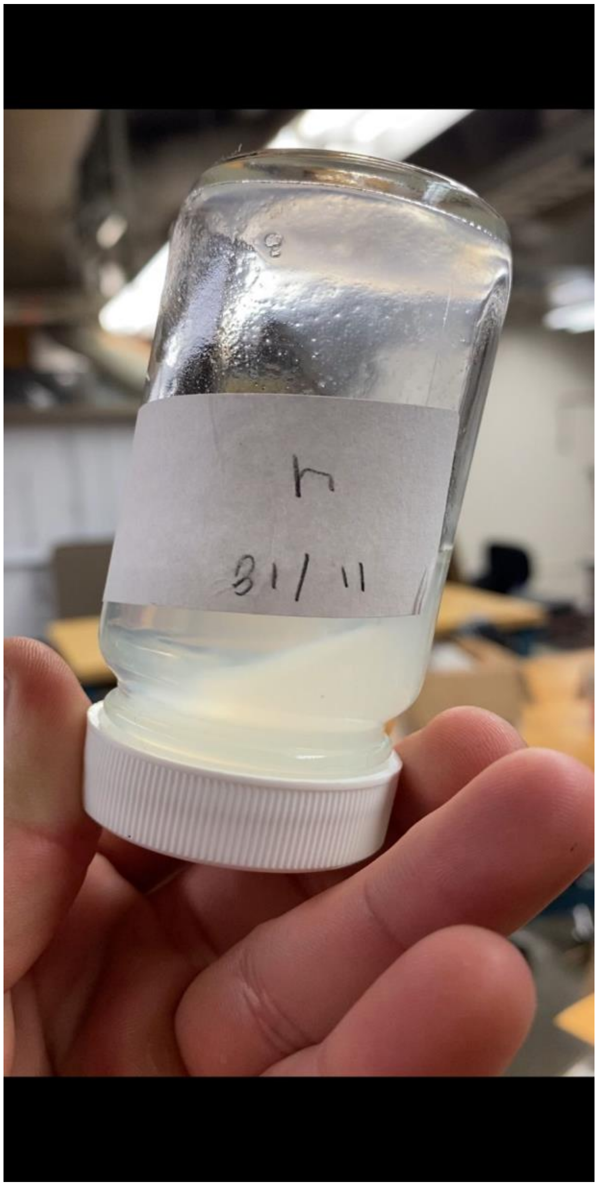


Figure 25. Sample 15 from table 5.

The experiments were analyzed after two weeks to see if they were stable in terms of their viscosities. The results are represented in tables 10, 11 and 12 as well as in figure 20. As it can be seen in the tables, the samples are very stable, and the viscosities remained the same for almost all cases with very few exceptions that more likely be due to an error while using the rheometer.

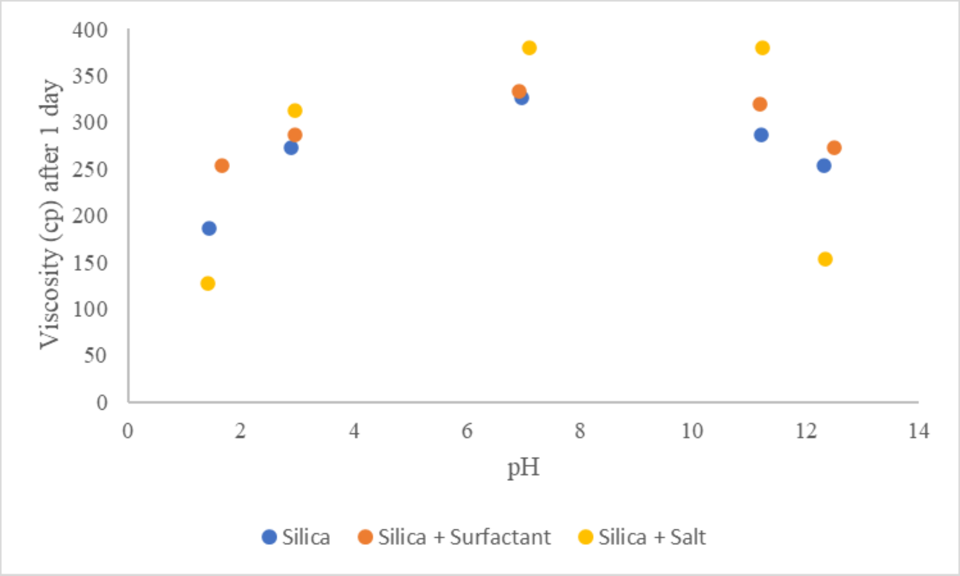


Figure 26. Experiments from tables 9, 10 and 11.

Table 10. Triplicate of 2.5 vol% silica nanoparticles without Bioterge AS-40 and without NaCl.

Type	Sample	pH	Vol % of silica nanoparticles	Viscosity (cP) after 1 hour	Viscosity (cP) after 2 hours	Viscosity (cP) after 24 hours	Viscosity (cP) after 14 days	Viscosity (cP) after 15 days	Viscosity (cP) after 16 days
Very acidic	1	1.42	2.5	100	120	180	180	180	180
	2	1.43	2.5	120	100	160	160	160	160
	3	1.48	2.5	160	160	220	220	220	220
Acidic	4	2.9	2.5	120	140	260	260	260	260
	5	2.93	2.5	120	140	280	300	300	300
	6	2.84	2.5	120	140	280	280	280	280
Neutral	7	6.9	2.5	140	180	320	320	320	320
	8	6.93	2.5	80	120	320	320	320	320
	9	7.1	2.5	140	160	340	340	340	340
Basic	10	11.3	2.5	80	100	280	300	300	300
	11	11.15	2.5	100	120	300	300	300	300
	12	11.16	2.5	120	160	280	280	280	280
Very basic	13	12.4	2.5	100	120	240	240	240	240
	14	12.21	2.5	80	100	260	260	260	260
	15	12.34	2.5	180	220	260	260	260	260

Table 11. Triplicate of 2.5 vol% silica nanoparticles with Bioterge AS-40 and without NaCl.

Type	Sample	pH	Vol % of silica nanoparticles	Amount of Bioterge AS-40 in mL	Viscosity (cP) after 1 hour	Viscosity (cP) after 2 hours	Viscosity (cP) after 24 hours	Viscosity (cP) after 14 days	Viscosity (cP) after 15 days	Viscosity (cP) after 16 days
Very acidic	1	1.71	2.5	5	160	160	240	240	240	240
	2	1.62	2.5	5	160	180	260	260	260	260
	3	1.66	2.5	5	140	160	260	260	260	260
Acidic	4	2.91	2.5	5	200	180	280	280	280	280
	5	2.98	2.5	5	180	220	300	300	300	300
	6	2.97	2.5	5	160	200	280	280	280	280
Neutral	7	6.91	2.5	5	200	220	340	340	340	340
	8	6.92	2.5	5	180	220	340	340	340	340
	9	6.96	2.5	5	180	200	320	320	320	320
Basic	10	11.16	2.5	5	180	200	320	340	340	340
	11	11.23	2.5	5	180	240	340	340	340	340
	12	11.14	2.5	5	220	240	300	300	300	300
Very basic	13	12.49	2.5	5	140	160	280	280	280	280
	14	12.47	2.5	5	200	200	300	300	300	300
	15	12.51	2.5	5	180	180	240	240	240	240

Table 12. Triplicate of 2.5 vol% silica nanoparticles with Bioterge AS-40 and with NaCl.

Type	Sample	pH	Vol % of silica nanoparticles	Amount of Bioterge AS-40 in mL	NaCl in grams	Viscosity (cP) after 1 hour	Viscosity (cP) after 2 hours	Viscosity (cP) after 24 hours	Viscosity (cP) after 14 days	Viscosity (cP) after 15 days	Viscosity (cP) after 16 days
Very acidic	1	1.45	2.5	5	1.25	100	120	160	160	160	160
	2	1.39	2.5	5	1.25	80	100	140	140	140	140
	3	1.42	2.5	5	1.25	100	100	120	140	140	140
Acidic	4	2.99	2.5	5	1.25	180	200	300	300	300	300
	5	2.94	2.5	5	1.25	260	280	340	340	340	340
	6	2.93	2.5	5	1.25	240	260	360	360	360	360
Neutral	7	6.92	2.5	5	1.25	260	360	420	420	420	420
	8	7.1	2.5	5	1.25	280	340	380	400	400	400
	9	7.08	2.5	5	1.25	300	360	420	440	440	440
Basic	10	11.25	2.5	5	1.25	240	320	380	400	400	400
	11	11.22	2.5	5	1.25	320	300	400	400	400	400
	12	11.18	2.5	5	1.25	280	340	400	420	420	420
Very basic	13	12.48	2.5	5	1.25	120	140	160	160	160	160
	14	12.42	2.5	5	1.25	100	100	200	200	200	200
	15	12.46	2.5	5	1.25	120	100	120	120	120	120

The experiments that were involved in lower volume % silica nanoparticles (1, 1.25, 1.5 and 1.75) are represented in tables 13, 14 and 15 as well as in figures 23 and 24. These set of experiments had problems in forming the gel at the same conditions (pH of 2.5-3,6.5-7 and 9.5-10). As shown in the pictures, it was noticed that the samples with lower vol % were not viscous enough to form a gel and even had problems in the reading of their viscosities using the rheometer. It is believed that by adding crushed Indiana limestone to the samples it would enhance the gelation process because its affinity to water molecules. However, the results were not as expected. More research needs to be done since the samples without crushed Indiana limestone were not much different from the ones with the latter.

Even though the addition of the Indiana limestone to the samples did not show any recordings of the viscosities, it visually showed that it helps the “gel” to form faster as 1/3 of the samples were found to be forming the gel after 1 day if compared with the other experiments in which only about ¼ of the samples formed a gel after 1 day. This can be confirmed by comparing sample 5 from table 15 with sample 9 from table 14. The difference is that the sample 5 from table 14 had the Indiana limestone and visually formed a gel after 1 day compared with sample 9 from table 13 did not have Indiana limestone added and did not form a gel after 1 day. It is safe to mention that the gel formed in these samples was not nearly as strong as the one formed with higher volume concentration of silica and the fluid was not viscous enough to record any viscosities in the rheometer. However, the texture of the samples seemed to be forming a gel. It is believed that the reason why no viscosity values were able to read in the rheometer with these samples is because the vol % of the silica nanoparticles was lower (1-1.75 compared to 2.5). Some of these samples looked like they had formed a gel but no viscosity measurement was recorded in the rheometer. Some other samples containing 2.5 vol % of silica nanoparticles with no added Indiana limestone did not form a gel but were able to show viscosity values using the rheometer.

Table 13. Different volume % silica nanoparticles without surfactant.

Type	Sample	pH	Vol % of silica nanoparticles	NaCl in grams	Viscosity (cP) after 1 hour	Viscosity (cP) after 24 hours	Gelation after 1 day	Gelation after 3 days
Acidic	1	2.57	1	1.25	N/A	N/A	No	No
	2	2.67	1.25	1.25	N/A	N/A	No	No
	3	2.54	1.5	1.25	N/A	N/A	No	Yes
	4	2.57	1.75	1.25	N/A	N/A	No	Yes
Neutral	5	6.68	1	1.25	N/A	N/A	No	Yes
	6	7.02	1.25	1.25	N/A	N/A	No	Yes
	7	7.09	1.5	1.25	N/A	N/A	No	No
	8	7.36	1.75	1.25	N/A	N/A	No	No
Basic	9	10.15	1	1.25	N/A	N/A	No	Yes
	10	9.8	1.25	1.25	N/A	N/A	No	Yes
	11	9.88	1.5	1.25	N/A	N/A	Yes	Yes
	12	9.69	1.75	1.25	N/A	N/A	Yes	Yes

Table 14. Different vol% silica nanoparticles with surfactant Bioterge AS-40.

Type	Sample	pH	Vol % of silica nanoparticles	NaCl in grams	Amount of Bioterge AS-40 in mL	Viscosity (cP) after 1 hour	Viscosity (cP) after 24 hours	Gelation after 1 day	Gelation after 3 days
Acidic	1	2.81	1	1.25	5	N/A	N/A	No	No
	2	2.75	1.25	1.25	5	N/A	N/A	No	No
	3	2.79	1.5	1.25	5	N/A	N/A	Yes	Yes
	4	2.91	1.75	1.25	5	N/A	N/A	No	Yes
Neutral	5	7.08	1	1.25	5	N/A	N/A	No	Yes
	6	6.89	1.25	1.25	5	N/A	N/A	No	Yes
	7	7.18	1.5	1.25	5	N/A	N/A	Yes	Yes
	8	7.2	1.75	1.25	5	N/A	N/A	Yes	Yes
Basic	9	9.82	1	1.25	5	N/A	N/A	No	Yes
	10	9.85	1.25	1.25	5	N/A	N/A	No	Yes
	11	9.56	1.5	1.25	5	N/A	N/A	No	Yes
	12	9.68	1.75	1.25	5	N/A	N/A	Yes	Yes

Table 15. Set of experiments with added crushed Indiana limestone.

Type	Sample	pH	Vol % of silica nanoparticles	NaCl in grams	Added crushed Indiana limestone in grams	Amount of Bioterge AS-40 in mL	Viscosity (cP) after 1 hour	Viscosity (cP) after 24 hours	Gelation after 1 day	Gelation after 3 days
acidic	1	2.57	1	1.25	5	5	N/A	N/A	No	No
	2	2.78	1	1.25	5	0	N/A	N/A	No	No
neutral	3	7.58	1	1.25	5	5	N/A	N/A	No	Yes
	4	7.85	1	1.25	5	0	N/A	N/A	No	Yes
basic	5	9.85	1	1.25	5	5	N/A	N/A	Yes	Yes
	6	9.75	1	1.25	5	0	N/A	N/A	Yes	Yes

Figure 27. Sample 2 from table 12.

Figure 28. Sample 2 from table 13.

Figure 29. Sample 2 from table 14.

The last set of experiments was performed as represented in table 16. Here, a set of 2.5 vol% of silica nanoparticles with surfactant is compared to a set of 2.5 vol% of silica nanoparticles without surfactant. Both experiments consisted of salt and a 15 wt% HCl was added with a small sample of Indiana limestone. Also, in table 16 pure 15% HCl is being analyzed as a baseline case. The results can be seen in figures 26, 27 and 28. It was observed that right after the addition of Indiana limestone to the fluid, a rapid reaction between the HCl and Indiana limestone started to occur. It is believed that some of the minerals from the rock are separated due to the reaction, increasing the pH of the solution, and therefore enhancing gelation. The pH of the samples was analyzed. The pH of the fluid without surfactant was found to be 5.85 before adding 15wt% HCl. After adding the acid, it was found to be 0.74. After a couple of minutes, it increased up to 0.86. On the other hand, the pH of the fluid containing the surfactant was found to be 6.1 before adding acid. After the addition of the acid it was found to be 0.75. After a couple of minutes, it increased up to 0.78. The fluid containing surfactant Bioterge AS-40 and the one without it demonstrated similar results. However, the pH of the fluid without the surfactant increased faster after the addition of the acid and the rock whereas the pH of the fluid with the surfactant took longer. A gel did not form in both samples until 4 days after mix. Then, another sample was made only with 15% HCl as a baseline case. This is represented in table 12 and figure 15. The pH of this sample was 0.3. After the addition of the rock, the pH started increasing very fast. After 1 minute, the pH increased from 0.3 to 0.63. After 3 minutes it increased to 1.03. At 5 minutes it was at 1.15 and after 30 minutes it was found to be at 1.6. The addition of the fluid seems to strongly decrease the reaction rate between the rock and the acid. This makes sense because the amount of acid used in the samples with fluid it is significantly less concentrated than just pure 15% HCl.

Table 16. Set of samples with added 15 wt% HCl and Indiana limestone.

Sample	pH before acid	Vol % of silica nanoparticles	NaCl in grams	Amount of Biotergе AS-40 in mL	pH after 5 mL of HCl and rock are added	pH after 5 mL of HCl are added after 3 minutes.	pH after 5 mL of HCl are added after 10 minutes.	pH after 5 days	Gelation after 1 day	Gelation after 4 days
1	5.85	2.5	1.25	0	0.74	0.85	0.86	5.13	No	Yes
2	6.1	2.5	1.25	5	0.75	0.78	0.78	5.21	No	Yes
3	0.3	0	0	0	0.3	1.03	1.26	N/A	No	No

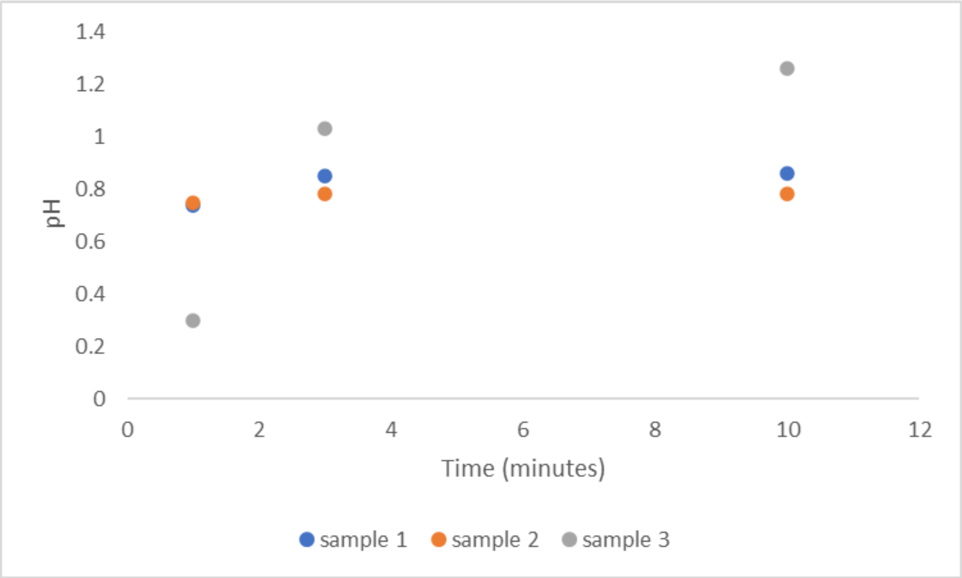


Figure 30. pH vs time graph for table 15 and 16 experiments.

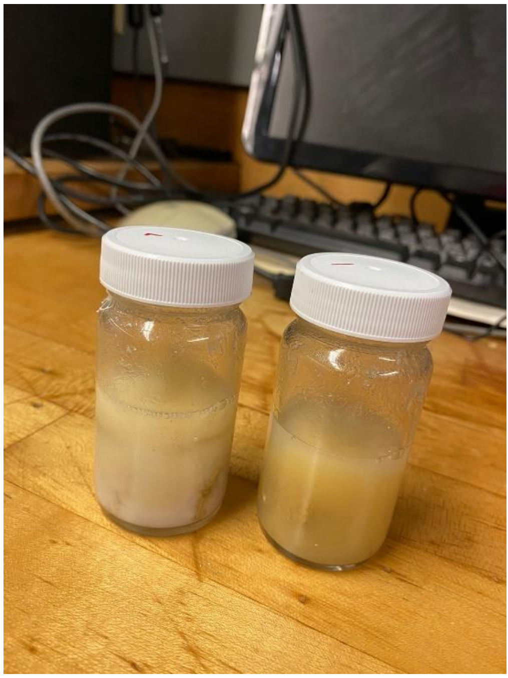


Figure 31. Samples from table 10.

Figure 32. Samples from table 11.

Figure 33. Sample from table 12.

Coreflood experiments for acidizing

Hydraulic oil was utilized to displace the nanofluid and the Indiana limestone. (1 inch by 1.5 inches) Figure 13 show the setup for a coreflood experiments. The nanofluid system is made of 2.5 vol% silicon dioxide nanopowder mixed with 3wt% NaCl in 15 wt% HCl. The most important thing to evaluate in the coreflood experiments is how the nanofluid propagates into the rock when a fluid with a high volume % (2.5 vol %) is injected with 15% HCl. One hypothesis is that if the nanofluid is injected with HCl, the acid would create wormholes in the rock and the nanoparticles would be moved into a high flow channel.

Test A is represented in table 17 and it was performed with Indiana limestone cores at 1100 psi back pressure. In test A, only 15 wt% hydrochloric acid was injected as a baseline case. The injection pressure was around 1235 psi and the difference in pressure, dp, across the core was about 100 psi. A picture of the inlet and oulet core sample is seen in figure 29 and 30. As it can be seen by visual observation, a wormhole is found in the inlet core sample and a very tiny wormhole is also seen right in the middle in the outlet core sample. The results from the coreflood apparatus are shown in table 18 and a graph representing the differential pressure vs time can be found in figure 31.

Table 17. First set of experiments for coreflood acidizing.

Test	A	B
Nanoparticle	0	2.5 vol% of hydrophobic silica nanoparticles solution in deionized water
NaCl	0	3wt%
Surfactant	0	0
HCl Concentration	15wt%	15wt%
pH	0.3	0.74
Flow rate (ml/min)	5	5
Pressure / dp (psi) at the end of the injection	0	0
Injection time (min)	25:31	34:00
Backpressure (psi)	1200	1150
Overburden pressure (psi)	500	500
Temperature (C)	25	25
Max upstream (psi)	1235	1200

According to the flow rate utilized in the coreflood experiments, the shear rate during the experiment and the contact time of the fluid with the rock were calculated.

$$Q = vA$$

$$\frac{V}{t} = vA$$

$$v = \frac{V}{At}$$

$$A = \pi r^2$$

Where,

Q = volumetric flow rate (cm^3/s)

v = velocity of the fluid (cm/s)

t = time (s)

A = cross-sectional area of the pipe (cm^2)

$$v = \frac{0.08333}{(1)(\pi)(0.3715)^2}$$

v = 0.2631 cm/s

Since,

$$\gamma = \frac{v}{d}$$

Where,

d = distance (cm) or length of the pipe

v = velocity of the fluid (cm/s)

γ = shear rate (s^{-1})

$$\gamma = \frac{0.2631}{162.56}$$

$\gamma = 1.618 \times 10^{-3}\ s^{-1}$

Since the sample length was 1.5 inches or 3.81 cm, the contact time of the fluid with the rock was calculated as follows,

$$\frac{3.81}{0.2631} = 14.48\ seconds$$

The fluid propagates through the rock within 14.48 seconds.

Also, the permeability of the samples was calculated using the equation below.

$$k = \frac{(Q)(A)(\Delta P)}{(u)(L)}$$

Where:

Q = flow rate (mL/min)

ΔP = pressure drop (psi)

u = viscosity (cP)

L = length of the tube (in)

k = permeability of the sample (mD)

A = cross sectional area (in^2)

$$k = \frac{(5)(\pi)(0.3715^2)(75.26)}{(280)(6)}$$

k = 0.015 md

Figure 34. Test A core sample inlet.

Figure 35. Test A core sample outlet.

Table 18. Test A coreflood experiment data.

Test A				
Time (minutes)	Pressure (psi) 0-200 diffuser	Pressure (psi) 0-2000 diffuser	Pump pressure (psi)	Flow rate (ml/min)
0.5	0.74	0.9	80	5
1	1.01	1.2	80	5
1.5	2.02	2.3	80	5
2	2.94	3.2	81	5
2.5	4.26	4.4	82	5
3	5.51	5.6	84	5
3.5	6.68	6.7	85	5
4	8.37	8.4	87	5
4.5	10.54	10.5	89	5
5	12.3	12.2	92	5
5.5	15	15.1	94	5
6	17.62	17.7	96	5
6.5	20.57	20.3	101	5
7	24.09	24.1	105	5
7.5	27.98	27.8	110	5
8	33.35	33.2	115	5
8.5	38.05	37.8	121	5
9	42.58	35	120	5
9.5	43.62	44.9	124	5
10	46.7	45.8	133	5
10.5	53.34	52.7	142	5
11	61.53	61.1	151	5
11.5	70.29	70.2	161	5
12	78.87	78.7	170	5
12.5	86.69	86.6	178	5
13	93.21	93.1	188	5
13.5	98.03	98	191	5
14	99.73	99.8	192	5
14.5	99.58	99.7	194	5
15	99.44	97.8	195	5
15.5	94.28	94.1	197	5
16	90.04	90.7	200	5
16.5	83.99	84.4	206	5
17	76.85	78.1	217	5
17.5	68.03	68.8	236	5
18	58.54	59.8	275	5
18.5	48.74	50.4	342	5
19	40	41.8	451	5
19.5	31.62	33.3	650	5
20	22.82	26.1	1220	5
20.5	40.63	40.1	1227	5
21	78.3	84.6	1228	5
21.5	79.96	85.6	1230	5
22	82.33	87.7	1233	5
22.5	82.47	87.9	1235	5
23	88.73	88.1	1236	5
23.5	83.5	88.8	1236	5
24	84.69	89.9	1236	5
24.5	85.09	90.5	1235	5
25	85.92	91.3	1235	5
25.5	84.17	89.4	1235	5
26	86.68	96.2	1235	5
26.5	86.8	96.2	1232	5
27	87.24	92.2	1202	5
27.5	80.9	86.4	1149	5
28	52.12	57.1	1144	5
28.5	2.1	8	1192	5
29	0	4.7	1200	5

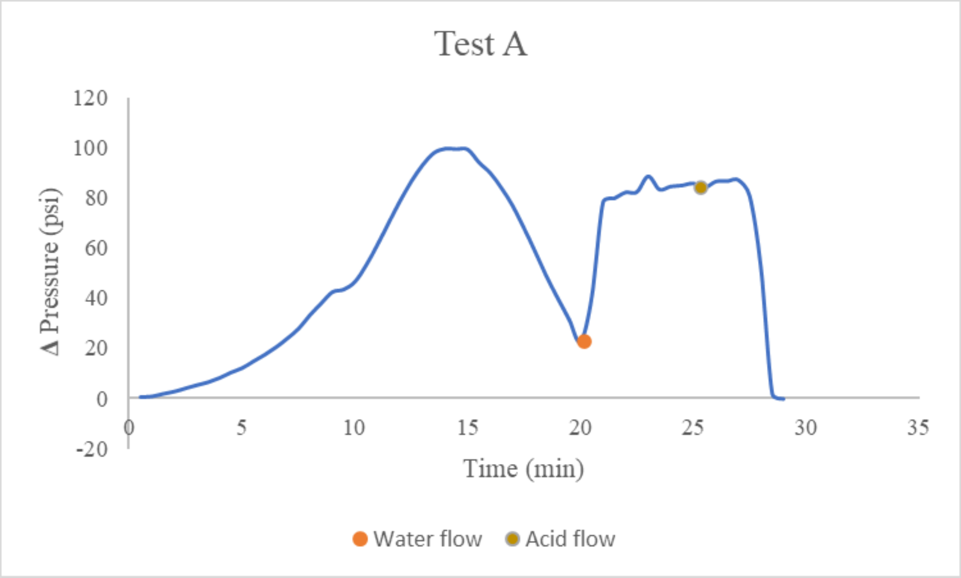


Figure 36. Test A – change in pressure vs time graph.

As it is shown in figure 31, a change in pressure vs time graph was made with the data collected. The graph shows that the propagation of the fluid through the rock was successful since the change in pressure reached 0 at some point. This can also be proved by looking at the core samples, it can be found that some wormholes are created, one wormhole is seen in the inlet and 3 small wormholes are found in the outlet, meaning that the fluid propagated successfully through that path. From minute 0 to 20 the pressure starts increasing as the rock is saturated with water. Then the pressure starts to decrease because is released by finding a way to pass through the rock sample. At minute 20:31 water started to come out, then the pressure started going up and at minute 25:31 the acid started to come out as the accumulators were switched. So, when it finally reaches 0 it means that the rock already has a path in which the fluid flows successfully. The acid flowed for 3:09 minutes from minute 25:31 to 28:40. The permeability of the sample was found to be 118029.334 md (before injection).

In test B, 2.5 vol % silica nanoparticles were utilized, and it was performed with Indiana limestone cores. The maximum pressure was around 1200 psi and the nanoparticles were successfully propagated through the core with 0 psi of difference in pressure. The propagation of the nanofluid was successful because the difference in pressure reached 0 but it cannot be confirmed by visual observation as it is shown in figure 32 and 33. This can be because since the fluid is not as strong as pure 15% HCl it does not penetrate the rock as easy as the pure acid. That is the reason why test B took 5 more minutes to be completed and the change in pressure was more unstable compared to the one in test A. Something that could have been better was to try a higher flow rate as this would help in the propagation of the fluid through the rock, but it could damage the core sample. The results from the coreflood apparatus are shown in table 19 and a graph representing the differential pressure vs time can be found in figure 25.

Figure 37. Test B core sample inlet.

Figure 38. Test B core sample outlet.

Table 19. Test B coreflood experiment data.

Test B				
Time (minutes)	Pressure (psi) 0-200 diffuser	Pressure (psi) 0-2000 diffuser	Pump pressure (psi)	Flow rate (ml/min)
0.5	0.98	1.2	75	5
1	1.74	2	77	5
1.5	2.79	3.1	78	5
2	3.93	4.1	80	5
2.5	5.37	5.4	81	5
3	6.66	6.8	82	5
3.5	8.47	8.5	83	5
4	9.64	9.7	84	5
4.5	10.86	11	86	5
5	12.16	12.3	88	5
5.5	13.11	13.4	90	5
6	14.1	14.3	91	5
6.5	14.91	15.1	91	5
7	15.51	15.7	93	5
7.5	16.03	16.1	95	5
8	16.35	16.3	96	5
8.5	16.36	16.5	97	5
9	16.27	16.4	98	5
9.5	16.14	16.2	99	5
10	18.61	18.2	99	5
10.5	19.2	19.1	100	5
11	18.74	18.8	101	5
11.5	17.93	18	102	5
12	17.38	17.4	103	5
12.5	16.9	17	106	5
13	16.52	16.6	109	5
13.5	16.17	16.2	111	5
14	15.83	15.9	115	5
14.5	10.49	10.7	114	5
15	13.9	13.8	120	5
15.5	16.05	16.1	126	5
16	17.35	17.5	132	5
16.5	17.92	18.1	138	5
17	17.69	17.9	147	5
17.5	16.86	17.2	150	5
18	15.83	162	173	5
18.5	14.94	15.4	191	5
19	12.87	13.6	220	5
19.5	12.57	13.4	261	5
20	11.16	12.4	340	5
20.5	10.91	12.6	950	5
21	8.09	11	680	5
21.5	14.5	19.4	1030	5
22	28.1	33.5	1158	5
22.5	26.62	32.1	1162	5
23	26.53	31.8	1176	5
23.5	28.37	31	1182	5
24	25.17	30.8	1188	5
24.5	26.68	32.2	1188	5
25	22.85	29.4	1188	5
25.5	22.9	28.3	1184	5
26	22.63	28.1	1187	5
26.5	22.08	27.4	1178	5
27	21.18	26.6	1183	5
27.5	20.82	27.4	1187	5
28	20.38	25.9	1180	5
28.5	21.67	27.1	1180	5
29	26.79	26.1	1180	5
29.5	16.14	21	1176	5
30	10.07	16.2	1171	5
30.5	6.63	12.2	1177	5
31	4.44	10.2	1186	5
31.5	3.33	9.4	1194	5
32	2.27	8	1189	5
32.5	1.78	7.4	1187	5
33	1.17	6.6	1195	5
33.5	0.92	6.9	1194	5
34	0.69	6.4	1197	5
34.5	0	5.8	1200	5

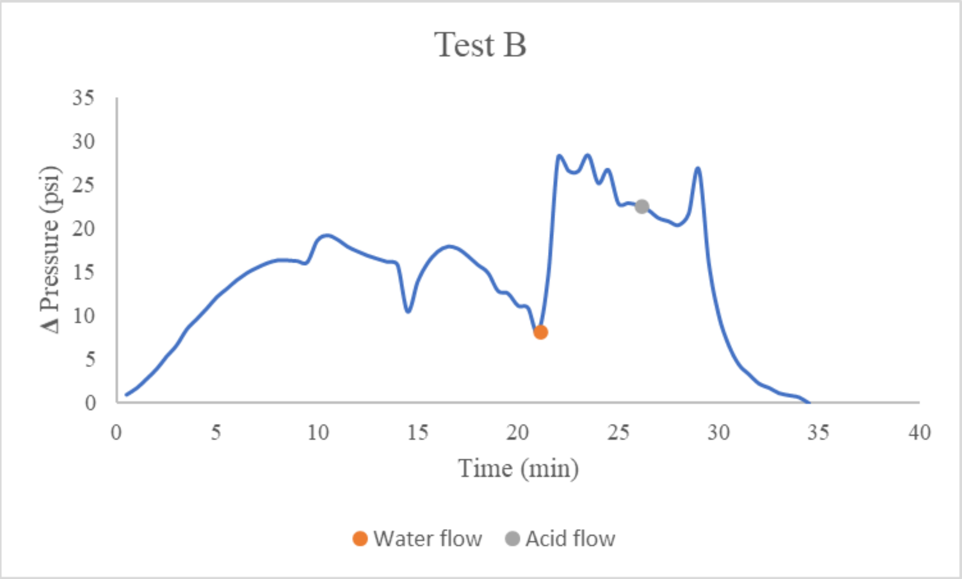


Figure 39. Test B – change in pressure vs time graph.

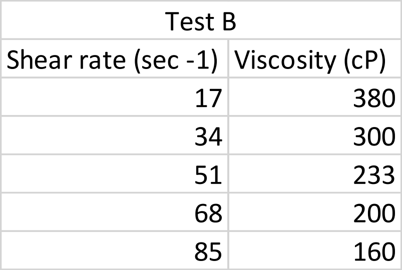
As it is shown in figure 39, a change in pressure vs time graph was made for test B with the data collected. The graph shows that the propagation of the fluid through the rock was successful since the change in pressure reached 0 at some point. Unfortunately, this can be proved by just looking at the core samples since there are no wormholes found. From minute 0 to 20 the pressure starts increasing as the rock is saturated with water. Then the pressure starts to decrease because is released by finding a way to pass through the rock sample. At minute 21:15 the water started to come out. Then, acid started to come out at minute 26:15. The test was completed at minute 34:00 when the difference in pressure reached 0. The acid flowed through the rock for 7:45 min from minute 26:15 to 34:00. The permeability of the sample was found to be 118029.334 md (before injection).

The viscosities of these set of experiments were analyzed. It was found that it is a shear thinning fluid as the viscosity started to decrease when the shear rate increased. This is shown in figure 35. It also exhibited non-Newtonian behavior as the samples showed different viscosities when shaken.

Something unusual was found during experiments A and B. It was found that the pressure difference in test A (pure HCl) was greater than the pressure difference in test B (HCl + silica). This should have not been the case because pure HCl has a viscosity value close to 1 cP whereas the fluid injected in test B had a viscosity of 120 cP. Test B being a more viscous fluid should have required the coreflood apparatus to build more pressure to propagate through the rock. The pressure drop difference between these tests could be caused by a human error. After test A was done there could have been a mistake in tightening the system when placing the new limestone sample and therefore producing a small leak that was not detected with human eyes.

It was seen that test A (pure HCl) took only 3 minutes to propagate through the rock whereas test B (HCl + silica) took 8 minutes to propagate the rock. This can be explained because pure HCl has more dissolving power than HCl combined with the fluid. This was also proven in some of the experiments when the pH change between pure HCl was reacting with Indiana core samples and fluid containing HCl and silica was reacting with Indiana core samples. It was seen that pure HCl dissolved the rock way faster and therefore had a greater reaction rate than HCl with silica. It can be concluded that it is easier for pure HCl to damage the rock and propagate compared to a combination of HCl and silica when the same volume of both fluids is applied.

Table 20. Test B rheometer data.



Test B	
Shear rate (sec -1)	Viscosity (cP)
17	380
34	300
51	233
68	200
85	160

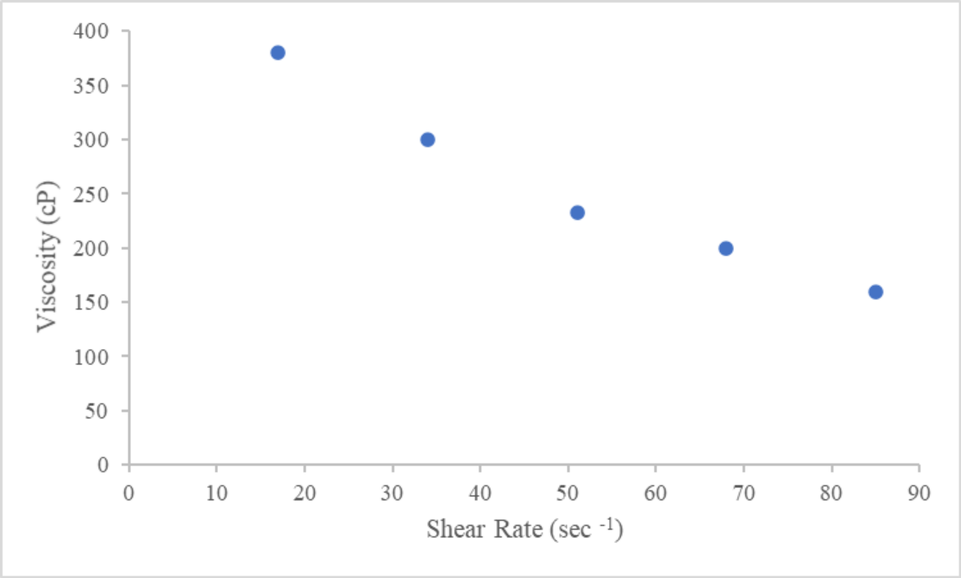


Figure 40. Test B Viscosity vs Shear Rate graph.

CHAPTER IV

CONCLUSIONS

In this research study, it was observed that the best conditions to create a gel are at a neutral pH and at a basic pH between 7-11.3 at which the gel was formed within one day. This is with a relatively high volume % of silica nanoparticles (2.5 vol%). The addition of the surfactant Bioterge AS-40 did not really show much difference to the samples without the surfactant. On the other hand, the addition of NaCl increase the viscosity values significantly.

Experiments for coreflood injection such as test A and B were performed with Indiana core samples at 1100 psi back pressure. In test A, only 15 wt% hydrochloric acid was injected as a baseline case. The injection pressure was around 1235 psi and the difference in pressure, dp, across the core was about 100 psi. As it can be seen by visual observation, a wormhole is found in the inlet core sample and a very tiny wormhole is also seen right in the middle in the outlet core sample. The graph shows that the propagation of the fluid through the rock was successful since the change in pressure reached 0 at some point. The pressure starts increasing as the rock opposes resistance when the fluid is trying to penetrate it. The rock is first saturated with water and then with acid. When the pressure difference in the transducer finally reaches 0 it means that the rock already has a path in which the fluid flows successfully.

In test B, the maximum pressure was around 1200 psi and the nanoparticles were successfully propagated through the core with 0 psi of difference in pressure. The propagation of the nanofluid was successful because the difference in pressure reached 0 but it cannot be confirmed by visual observation since no wormhole could be found. This can be because since the fluid does not have the same dissolving power as pure 15% HCl it does not penetrate the rock as easy as the pure acid. That is the reason why test B took 5 more minutes to be completed and the change in pressure was more unstable compared to the one in test A. The graph shows that the propagation of the fluid through the rock was successful since the change in pressure reached 0 at some point.

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BIOGRAPHICAL SKETCH

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