PERFORMANCE OF DIFFERENT ACIDS WITH VARIOUS FORMULATIONS FOR SANDSTONE FORMATIONS (TERENGGANU SAND)

by

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Dissertation submitted in partial fulfillment of the requirements for the
Bachelor of Engineering (Hons) Degree in Petroleum Engineering

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Program
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PETROLEUM ENGINEERING

Approved by,

____
(AP Aung Kyaw)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
June 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

TIRZA HAHIJARY

ABSTRACT

This report summarizes an experimental work about various acid used in sand acidizing by saturating the core sample, including the literature review, the methodology, and the result achieved from the experiment. As acidizing method has been used for many years in oil and gas wells, it is expected to improve the performance of the core sample, which in this case is taken from sandstone formation.

The objective of this project is to determine the most effective acid formulation that increases the core properties the most, especially the permeability. Ten cores are prepared from sands sample taken from Paka Beach, Terengganu, Malaysia. Analyzing the core properties i.e. porosity and permeability will be done beforehand followed by trial-and-error experiment in Core Analysis Lab in Universiti Teknologi PETRONAS, Malaysia. This project only focuses in matrix acidizing method for sandstone formation, whereby the core will be saturated with various acid formulations. The approach for the experiment is unusual compare to common acidizing treatment as the equipments are limited in the lab.

The literature review involved are mostly about sand acidizing, types of acids used in general, and stages of acidizing. All is summarized from open journals found in the internet and other sources i.e. books, thesis, etc. Methodology to achieve the project objective is also given, which consists of research methodology, project activities, experiment methodology, key milestone, and project Gantt chart. The result and discussion for this project will be elaborated and conclusion will be at the end of the report.

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My deepest gratitude goes to AP Aung Kyaw, my supervisor who has guided me and found time in a very busy schedule to give me knowledge and support, monitor my progress and answer my questions.

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CHAPTER 1

INTRODUCTION

1.1.Background

Oil and gas, known as hydrocarbons, are produced from thousands of meters underground. They are accumulated inside a rock formation that has good porosity and permeability. From the rock pores, they flow through the channels in between the pores, going to the production tubing, and finally up to the surface. In the early years of production, the flow rates of these hydrocarbons produced is promising due to naturally high porosity and permeability of the reservoir, also because of the pressure difference between the reservoir pressure and the bottom-hole pressure. However, the production is going to decrease over time due to several cause i.e. near-wellbore formation damage, clays that swells or migrates then clot the pore spaces, reservoir pressure declines, etc.

Acidizing treatment is a common and recommended method which has been used for many years to improve hydrocarbon production after some production time. **Figure 1** shows a graph of Nigerian oil well after mud-acid (HCl 12% + HF 3%) and hydrofluoric (HF) acid treatment. This figure shows that mud-acid does not give much increment in terms of production rate but on the other hand, HF gives significant recovery for the field. This fact proves that the correct acid combination for a particular field will increase the production of hydrocarbons.

Different types of acidizing treatments were developed i.e. matrix acidizing, fracture acidizing, acid washing, etc. For sandstone formation, matrix acidizing should remove the damage or plugged pores near the wellbore area so that the initial permeability will be attained or even gets higher to produce more hydrocarbons.

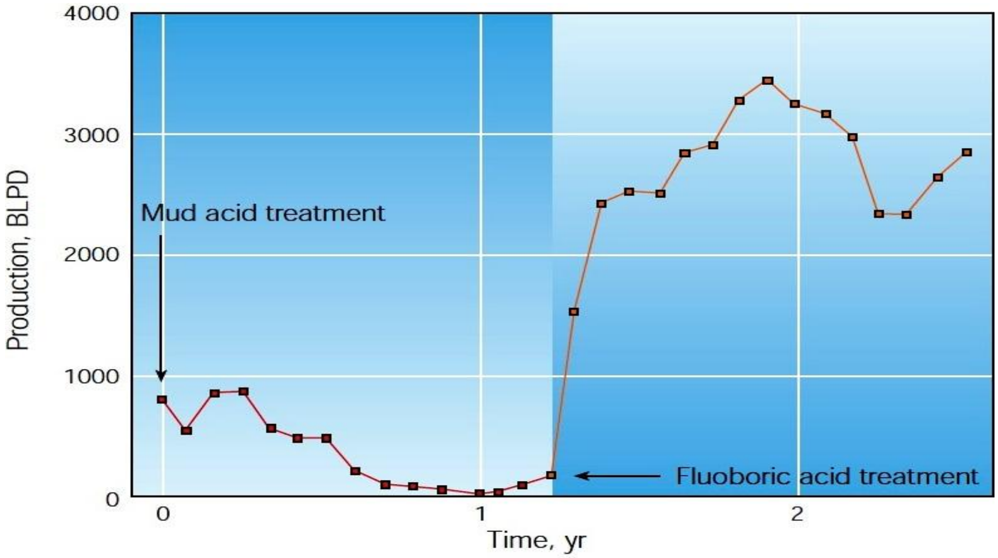


Figure 1: Production improvement after hydrofluoric (HF) acid treatment.

Field Overview

The cores are prepared by mixing sand sample taken from Paka Beach, Terengganu with Epoxy Resin and Hardener (9:1 ratio). Paka area is located around 100 km south Kuala Terengganu, the capital state of Terengganu, Malaysia, and it is facing the South China Sea. The location of Paka Beach is shown in **Figure 2** below (label A). Although Terengganu is a well-known area for its offshore hydrocarbons production, there is no record of oil and gas produced from Paka Beach. Yet the project will still be continued as its main purpose is to find the most suitable acid formulations to improve the properties of the particular formation.

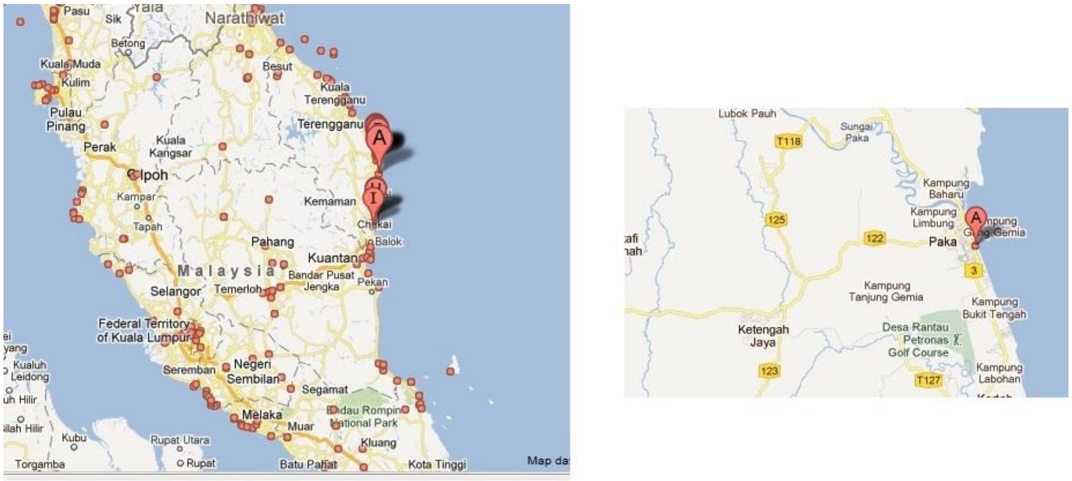


Figure 2: Paka Beach location

1.2.Problem Statement

The production of hydrocarbons is decreasing over time. This phenomenon may happen because of few reasons such as near-wellbore formation damage, increased skin factor, dissolved mineral into the pore spaces, etc. All the above reasons will decrease the initial porosity and permeability of the formation which later on will decline the production.

Matrix acidizing is the first recommended method to fix this problem. Yet, the process of acidizing is unique for each formation and can’t be generalized. Factors that affect this condition are formation history (how it was shaped), formation location (anticline, dome, etc), and acidizing history (whether there was an acidizing treatment had been applied into the formation or not). More damage to the formation will occur if the acid used is not compatible with each other or with the formation or formation fluids. By evaluating the core sample taken from the wellbore (formation lithology, solubility, mineralogy, etc), then only we may choose the method to optimize the production.

In this project, there are constrains met along the way. The unavailability of equipments and materials in the lab limit the experiment to be similar with ones that have been done in the industry. Few of the restrains are the sample is not from a real formation, there is no equipment for injecting the acids, and there is no gas available for the SEM machine to identify the mineralogy of the cores. Yet, the experiment will still be continued as its purpose is to find the most suitable and effective acid formulations that increases the properties of the rocks, especially permeability also porosity.

1.3. Objectives and Scope of Study

The main objective of this project is to determine the most effective acid formulation that increases the core properties the most, especially permeability. When the permeability increases, the fluid will ease to flow through the connected pores and consequently will increase the production rate in the real formation through the production tubing up to the surface. Yet, few prior points that have to be taken account are:

1. To analyze the initial properties of the core (porosity and permeability).
2. To do a trial-and-error experiment that will test the effect of various acid formulations to the core.
3. To find out the most suitable acid formulation that will increase the core performance the most, especially permeability.

The scope of study includes:

- Conducting research, experiments, calculations and/or simulation regarding matrix acidizing to determine acid formulations for sand formation taken from Paka Beach, Terengganu.
- The cores are saturated with different acid formulations since there is no equipment available for injecting the acids in the lab.
- Will be using conventional acid systems (HCl, HF, or the combination) and boric acid only.

CHAPTER 2
LITERATURE REVIEW

2.1. Acidizing Treatment

Acidizing is one of the way to optimize oil and gas production. It is now believed as the most widely used method for stimulation and workover practices in oil and gas industry.

Sandstone acidizing started in May 1933 by Halliburton. Hydrochloric (HCl) and Hydrofluoric (HF) acid were pumped to 1,532 feet deep well with 11 ft of open-hole production interval belongs to the King Royalty Company, Texas. The details of HF composition and strength mixture are not known. Yet, the result of this acidizing treatment was not giving good outcome and caused substantial sand production into the wellbore.

On the other hand, Jesse Russell Wilson from Standard Oil Company of Indiana was successfully pumping HF to sandstone formation on March 1933 which results in more discovery of the use of HF. Based on Wilson's findings, acid-removable formation damage due to solids plugging is remarkable by treating the formation with HF acid. Few experiments were conducted regarding combination of acids used in sandstone formation, i.e. Dowell who introduced *mud acid* which is the combination of 12% HCl – 3% HF in 1939, also Smith and Hendrickson who elaborated HF reactivity and others effects in the field, etc. Since then, many matrix acidizing treatments has been performed since the mid of-1960s. Acetic and formic acids also have been used, in combination with HF.

There are three common methods of acidizing which are acid washing, matrix acidizing, and acid fracturing. The main aim of these three methods is to improve the production of hydrocarbon fluids by removing formation damage caused by drilling or workover operations near-wellbore area. The mechanism of the treatment is by pumping and injecting acid formulations to dissolve into the formations and to achieve specific purposes i.e. penetrating the reservoir, creating wormholes, removing near-wellbore damage, washing the reaction products, etc (different formation has different approach and intention of acidizing treatment).

In this project, matrix acidizing method will be applied by saturating the core sample taken from sandstone formation. In sandstone formation, matrix acidizing treatment should be designed primarily to remove or dissolve acid-removable damage or plugging in the perforations and in the formation pore network near the wellbore[8]. The acid supposed to flow along and through the pores, dissolving solids and fines occupies in the pore throats and space that restrict the flow of oil or gas. **Figure 3** shows how the acid flows in sandstone pores system. In short, matrix acidizing is a formation damage removal treatment for sandstone formations. This will only succeed when the formation is damaged. If it is not, the treatment cannot be expected to increase the production significantly. Formation damage may occur during drilling, cementing, perforating, production, workover, and stimulation.

Figure 3: Acid flows through a sandstone matrix pore system

It is important to understand the skin term occurs in the formation then followed by the well production rate. Skin (s) is a mathematical expression of the damage present, where flow rate (q) is expressed from Darcy’s law which is directly proportional to permeability (k). Permeability and skin factor are the most importance variable in stimulation design. These two are preferably measured before and after stimulation, although sometimes is not practical due to cost constrained. Following aspects have to be investigated before treating the formation damage:

- Reservoir geology and mineralogy
- Reservoir fluids
- Production history
- Drilling history (e.g. fluids used)
- Cementing program (e.g. cement bond logs)
- Completion and perforation reports (e.g. fluids used)
- Workover history
- Stimulation history

Skin factor:

$$s = \frac{k}{k_{s-1}} \ln \frac{r_s}{r_w}$$

Production rate:

$$q = \frac{7.082kh(p_s - p_{wf})}{B\mu \ln\left({}^{r_e}/_{r_s}\right) + s}$$

2.2. Types and Stages of Acid System

There are two types of acid systems which are:

1. *Conventional Acid Systems* (HCl, HF, CH_3COOH, HCOOH, etc)
2. *Retarded Acid Systems* (gelled acids, chemically retarded acids, emulsified acids).

The use of acid systems in each formation is different from one another based on reservoir behavior and characteristic, also purposes of the treatment. For example, the concentration of acids pumped into sandstone and carbonate formation is different. Other example based on the types of acid systems is Conventional Acid Systems is usually used to dissolve and react with rock matrix to achieve certain goal i.e. increase permeability and creating flow channel for fluid to move. On the other hand, Retarded Acid Systems, as it is called, is generally being applied to slow or retard the acidizing process because the acid has penetrated too far from the initial plan and somehow causes problems. This is usually being done by pumping high viscosity fluid to reduce the acid transfer rate inside the rock matrix. **Figure 4** is the micrographs result of pore-filling clays before and after exposure of mud acid (HCl 12% + HF 3%) and hydrofluoric (HF) acid. It shows that after acid is being pumped into the core sample (right micrographs), the clays that filled the pore spaces before (left micrographs) is lessen which will increase back the porosity and permeability, as well as the production.

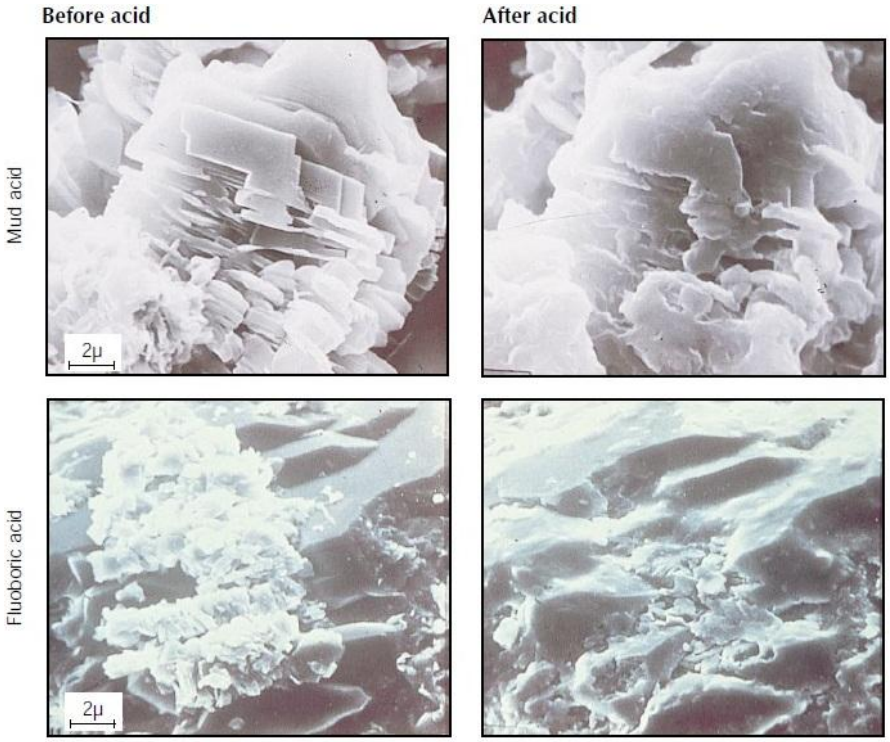


Figure 4: SEM micrographs

HCl and HF have been the most common acids used in the industry. HF is the only acid that dissolves siliceous minerals significantly. Thus mixing HF with other acid (HCl, or boric acid) is a regular treatment to get major improvement in permeability. The most frequent mixtures used are HCl and HF (mud acid). The concentration of both acids used are varied from the low end (e.g. HCl 3% and HF 0.5%) to the high end (HCl 12%-15% and 3%-5% HF, or more). For sandstone with high carbonate mineral content (>15%-20%), the mixture of HCl-HF should be avoided. But, carbonates are likely present as grain cementation in sandstones and by removing it could diminish rock competence. Modern HF acid systems with low total acidity (mild pH) are a good option in such cases because it reacts slowly with the carbonates.

Besides HF, HCl is also applicable for removing certain minerals, such as $CaCO_3$, $FeCO_3$, FeO_2, and FeS_2. Acetic acid and formic acids, which usually are called *organic acids*, are sometimes used to replace HCl, especially in high-temperature conditions, where HCl can cause severe corrosion.

For matrix acidizing, there are 3 stages involved in the treatment:

1. *Pre-flush stage*, to "clean and prepare" the pores without making any damages or factures i.e. to dissolve with any carbonates if presents and to remove formation waters with high concentration of calcium to avoid precipitation.
2. *Main stage*, to remove skin damage, to prevent further fines migration, to enlarge pores spaces, etc
3. *Post-flush stage*, to displace the reaction products.

In sandstone formation, there are four main categories of minerals: silica (quartz) - the main mineral, feldspars, clays, and carbonates, whereas typical acid that are generally used consists of 15% hydrochloric (HCl) acid as pre-flush fluid and mud acid (HCl 12% and HF 3%). The reaction of mud acid keeps the pH low and prevents detrimental precipitation. Mud acid also dissolves in siliceous materials and clays. Injecting hydrofluoric (HF) acid alone is highly not recommended for sandstone formation with high carbonate content because it can results in CaF_2 precipitation.

Retarded hydrofluoric-based acid (RHF) is also sometimes used in stimulation for sandstone reservoir. The goal of RHF is to decrease the reaction rate of HF with clays and feldspars, to enhance acid penetration in the formation and to remove deeper formation damage. RHF is usually based on three acids which are:

1. Boric Acid (H_3BO_3)
2. Aluminum Chloride ($AlCl_3$)
3. Phosphoric Acid

All three listed acids above are the examples for hydrofluoric-based acid, means they can react with sandstone formation in the stimulation. For example, boric acid is the most common acid used to neutralize active hydrofluoric acid (HF). Moreover, when HF reacts with boric acid (H_3BO_3), the outcome will be fluoboric acid (HBF4). Equations 1 and 2 explain the reactions below.

Fast Reaction:

$$H_3BO_3 + 3HF \rightarrow HBF_3OH + 2H_2O \tag{1}$$

Slow Reaction:

$$HBF_3OH + HF \leftrightarrow HBF_4 + H_2O \tag{2}$$

As HF acid spends on siliceous minerals, HBF4 hydrolyzes to regenerate HF (the reserve reaction of equation (2) [5]. **Table 1** portrays the solubility of sandstone minerals in HCL and HCL-HF.

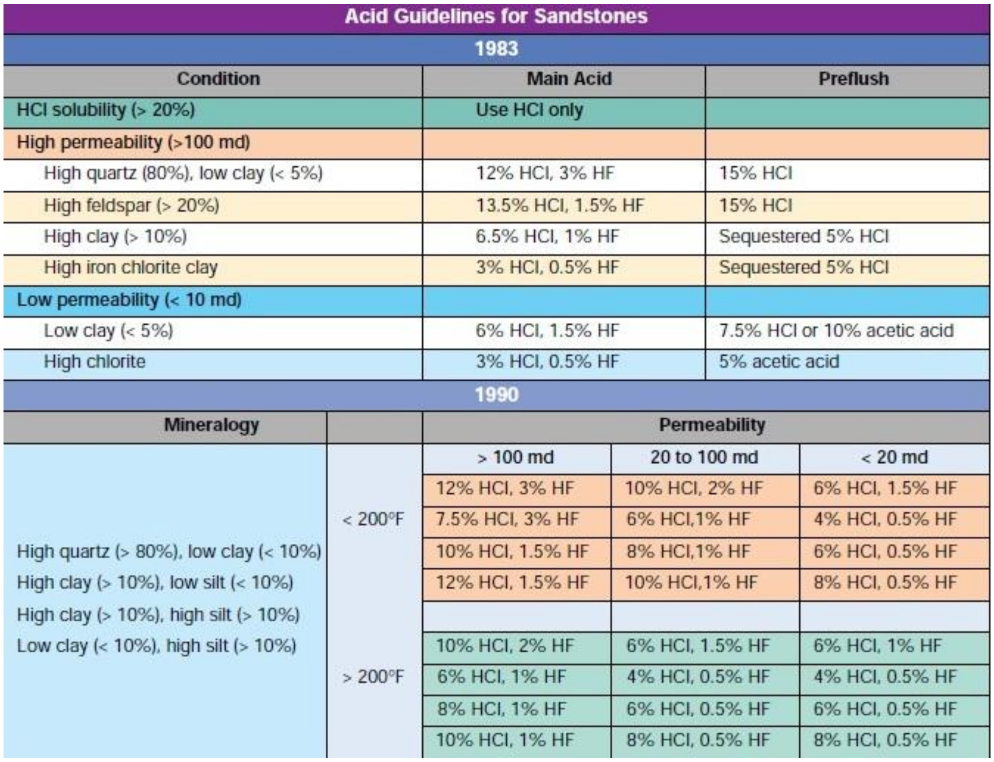
Mineral	Solubility in HCl	Solubility in HCl-HF
Quartz	Not	Very low
Feldspars	Low to moderate	Low to moderate
Clays	Not	High
Kaolinite	Not	High
Illite	Not	High
Smectite	Not	High
Chlorite	Low to moderate	High
Carbonates	High	High
Calcite	High	High
Dolomite	High	High
Ankerite	High	High
Slderite	High	High

Table 1: Sandstone minerals solubility in HCl and HCL-HF[8]

Although by injecting RHF makes the process more complex, RHF is less reactive and less damaging for the rock formation, thus results in deep penetration. From the study that had been done, RHF acids react rapidly with clay minerals and slowly with sand particles. The used of RHF decreases the dissolution of clays, but it also increases the soaking time by the precipitation. Concisely, retarded acid systems should only be used to remove deep formation damage.

Types and concentrations of acid injected into the formation depend on mineralogy and bottomhole pressure. Thus, information such as type and extent of formation damage, location of the reservoir, formation history, and mineralogy are very important elements before starting the acidizing treatment.

Table 2 shows the evolution of acid system guidelines for sandstone formation from year 1983 to 1990. From this table, the rule of acids formulations for sandstones formations is improving from time to time, especially in currents days. More detail guideline is available and open to the industry. Now, knowledge based systems incorporate hundreds of rules of fluid choice.



Acid Guidelines for Sandstones

1983

Condition	Main Acid	Preflush
HCl solubility (> 20%)	Use HCl only	
High permeability (>100 md)		
High quartz (80%), low clay (< 5%)	12% HCl, 3% HF	15% HCl
High feldspar (> 20%)	13.5% HCl, 1.5% HF	15% HCl
High clay (> 10%)	6.5% HCl, 1% HF	Sequestered 5% HCl
High iron chlorite clay	3% HCl, 0.5% HF	Sequestered 5% HCl
Low permeability (< 10 md)		
Low clay (< 5%)	6% HCl, 1.5% HF	7.5% HCl or 10% acetic acid
High chlorite	3% HCl, 0.5% HF	5% acetic acid

1990

Mineralogy		Permeability		
		> 100 md	20 to 100 md	< 20 md
High quartz (> 80%), low clay (< 10%) High clay (> 10%), low silt (< 10%) High clay (> 10%), high silt (> 10%) Low clay (< 10%), high silt (> 10%)	< 200°F	12% HCl, 3% HF	10% HCl, 2% HF	6% HCl, 1.5% HF
		7.5% HCl, 3% HF	6% HCl,1% HF	4% HCl, 0.5% HF
		10% HCl, 1.5% HF	8% HCl,1% HF	6% HCl, 0.5% HF
		12% HCl, 1.5% HF	10% HCl,1% HF	8% HCl, 0.5% HF
	> 200°F	10% HCl, 2% HF	6% HCl, 1.5% HF	6% HCl, 1% HF
		6% HCl, 1% HF	4% HCl, 0.5% HF	4% HCl, 0.5% HF
		8% HCl, 1% HF	6% HCl, 0.5% HF	6% HCl, 0.5% HF
		10% HCl, 1% HF	8% HCl, 0.5% HF	8% HCl, 0.5% HF

Table 2: Evolution of acid system guidelines for sandstone formation

2.3. Acidizing Damage Mechanisms

Acids combination can cause risks such as fines migration, precipitation of reaction products, and rock deconsolidation. These risks could be minimized by pumping the right volume and concentrations of acids.

Few mechanisms that could damage the formation are use of incompatible additives or improper mixing, re-precipitation of acid reaction products, loss of near-wellbore formation compressive strength, formation of emulsions and sludge, and post-treatment fines migration. Those mechanisms can cause severe damage to the formation and is sometimes irreversible. Thus, evaluating all formation characteristics is very crucial before applying acidizing treatment.

Precipitation usually occurs when HF is injected into the formation. This phenomenon sometimes has to be taken account for as the precipitate(s) would damage the formation more. Table 3 below shows the precipitation of HF in sandstone formation

Reaction	**Precipitate(s)**
HF + carbonates (calcite, dolomite)	Calcium and magnesium fluorides (CaF_2, MgF_2)
HF + clays, silicates	Amorphous silica (orthosilicic acid, $H_4Si(OH)_4$)
HF + feldspars	Sodium and potassium fluosilicates (Na_2SiF_6, K_2SiF_6)
HF + clays, feldspars	Alumunium fluorides (AlF_n^{3-n}), aluminum hydroxides
HF + Illite	$Na_2SiF_{6,}$ K_2SiF_6
Spent HF + formation brine, seawater	$Na_2SiF_{6,}$ K_2SiF_6
HCl-HF + iron oxides and iron minerals	Iron compounds
HF + calcite (calcium carbonate)	Calcium fluosilicate

Table 3: Damaging HF reactions in sandstones

Although precipitate(s) damage the formation, they are not completely avoidable, but they can be minimized by using proper fluid selection, modern acid system use, and treatment design.

It is also common in sandstone acidizing to have post-treatment fines migration. New fines and mineral may be generated by HF reaction, particularly clays and certain zeolites, although they rarely occur. The fines plug the pore throats and reduce permeability, instead of increasing it. This mechanism can be minimized by slowly bringing on the well and not maximizing return production right away. By doing this, the fines have less chances to accumulate at pore throats and restrict the flow of the fluids. It is called *a bottleneck*, or a traffic engineering problem.

Sandstone acidizing is only effective when formation is present. The right type of acid must be used to remove the damage. For example, when siliceous fines are present, HCl should not be used as it will not dissolve the plugging solids. On the other hand, HF should not be used to remove calcium carbonate ($CaCO_3$) solids or scales other than silica.

The correct volumes or concentration of acids is also as important as the acids choice. Some formations are very sensitive to volumes of acids, especially HF. High clay content in sandstone could be damaged by high-strength HF solutions by the re-precipitation of reaction products near wellbore. HCl can be very damaging to sandstones containing high levels of iron chlorite clay and certain zeolites[8].

In conclusion, three main points that have to be followed to have a successful sandstone acidizing treatment are:
1. Determine the correct candidate well for the stimulation.
2. Design an effective treatment.
3. Monitor the treatment for subsequent improvement.

All is begun by analyzing the well performance and reservoir properties, followed by determining whether skin damage is present; determine the appropriate fluids, acid types, concentrations, and treatment volumes; establish a proper treatment additive program; determine the treatment placement method; ensure proper treatment execution and quality control; and finally evaluate the treatment. In this way, the acidizing can be successful and the main objectives may be achieved.

CHAPTER 3
METHODOLOGY

3.1 Research Methodology

In order to achieve project objectives, some research is being done on acidizing treatment, especially matrix acidizing method using both conventional and retarded acid systems. Useful information is obtained from open journals and technical papers provided in the internet.

3.2 Project Activities

The overall project activities are shown in **Figure 5** below:

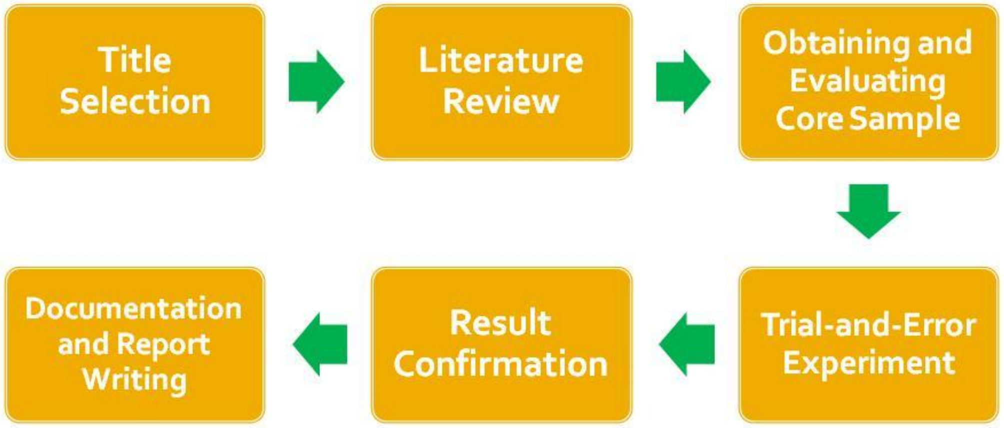


Figure 5: Project activities plan

During the first semester for Final Year Project (FYP-I), title selection, literature review regarding the study, and obtaining the sand sample from Paka Beach, Terengganu was done. The experiment starts on the second semester (FYP-II). The sand sample was compressed to a core and was evaluated in core analysis lab for its properties i.e. porosity and permeability.

With these data, the acidizing experiment may begin. The core was saturated in different acid formulations by trial-and-error experiment. By looking at the results later on, the acid formulation that improve the core's performance (especially permeability) the most will be selected. All procedures will be recorded and written down on the reports along the experiment and be finalized in Final Report or Dissertation.

3.3 Experiment Methodology

3.3.1 Apparatus

Sieve shaker, PVC pipes, Laboratory Weighing Scale, Rectangle Plastic Container, Coring Machine, Caliper, VINCI Poroperm, 50mL and 100mL plastic Measuring Cylinders, 600ml Plastic Beaker, Clamp, Plastic Desiccators, Blue Silica Gel, Pump, Fume Hood, Magnetic Stirrer, Hotplate, and Convection Oven.

3.3.2 Materials

Paka sands, Epoxy + Hardener (9:1 ratio), Pipe Water, Cements, Helium gas, Distilled Water, HCl 37%, HF 48%, and Boric Acid.

3.3.3 Procedures

This experiment consists of two main parts, before and after acidizing. The first part consists of molding the sand sample into ten cores for ten runs of experiments and tests the core initial properties (porosity and permeability) before acid saturation. The sand obtained from Paka is filtered using sieve shaker then 600 µm, 425 µm and 300 µm grains are chosen to be molded. The grains are mixed in PVC pipes with epoxy resin and hardener with 9:1 ratio, and then they are cemented to be drilled with coring machine to get the correct core size for poroperm machine. The porosity and permeability of all cores are tested using VINCI Poroperm apparatus by injecting Helium (He) gas. All experiments are run in room temperature and pressure, handled with serious precautions and personal protective equipment (PPE) as the acids used are corrosive and dangerous for any contact with body skin.

The second part of the experiment is saturating the cores with different acid formulations followed by testing the cores properties afterward. The cores are saturated inside a desiccators placed in a fume hood for 4 hours. Total solution for each experiment is 250ml of acid(s) including distilled water, calculated with molar formulas:

$$M_1V_1 = M_2V_2 \tag{3}$$

M_1 = concentration of the initial acid (HCl 37% or HF 48%)
V_1 = volume of acid required in the solution
M_2 = concentration of the required acid in the solution
V_2 = volume of total solution = 250ml

*Calculation for acid concentrations is attached in Appendix A

Scanning Electron Micrographs (SEM) is also being run before and after the saturation process. The purposes of SEM are to observe the reaction between acids and the core, and to analyze the permeability and porosity changes from the micrographs image. The machine used for SEM is “LEO 1430 UP” which utilized electric power, transferred to current, and turned into X-Ray energy. The cores have to be crashed into very small piece of rocks and be vacuumed first before they are put inside the SEM. The duration of SEM for each core is around 5-15minutes, depends on how many data and how details we want to investigate the core. We can also magnify the core in SEM for clearer and more specific picture of the grains.

3.3.3.1 Preparing the sands into the core sample

1. Dry the sands for 1 day until it feels waterless.
2. Filter the sands with sieve shaker for 10 minutes and take the 600 µm, 425 µm, and 300 µm size grains.
3. Mix 400gr of grains with 80ml of Epoxy resin + 8ml of hardener (9:1 ratio) in PVC pipes with diameter of 2 in. and 0.5 ft long pipe for 2 cores.
4. Repeat step-2 for another 4 pipes for total of 10 cores.

5. Wait until all cores harden for 2 days.

6. Cement the pipes in a square container and dry it for 2 days.

7. After the cement is hardened, take out the hardened cement, saw the PVC pipes to release the core, and then drill and trim the cores with desired diameter and length for Poroperm machine, which for this experiment is 1 in. diameter and 2 in. long.

3.3.3.2 Poroperm test

1. Put the core inside the suitable core holder according to its size, in this case is 1 in. holder. Tie all screws until they are tight.
2. Open the Helium (He) gas tank valve.
3. Set the confining pressure to 300 psi.
4. Run the software and wait for the result of both properties (porosity and permeability).
5. Write down all result.
6. Vent the confining pressure and unload the core from the holder.
7. Repeat step 1-6 to another 9 cores.
8. Close the He gas tank valve at each experiment.

3.3.3.3 Acid Saturation

1. Determine the desired volume of acid(s) and distilled water used using 50mL and 100mL plastic measuring cylinders. *The total solution for each experiment is 250ml with different combination and concentration of acids.*
2. Saturate each core in a 600ml plastic beaker inside closed desiccators (with blue silica gel at the bottom part) connected with pump in an active fume hood.
3. Turns on the pump inside fume hood for 30minutes then turn it off so there will be no free air inside the desiccators.
4. Saturate the core for 4hours.

5. Take out the core using the clamp, dry it with compressed air and put inside the oven for 12hours.

6. Take out the desiccators with all the connected pipes and then wash it.

7. Take out the core(s) from the oven and run the porosity and permeability test once again for after acid data.

Figure 6: Poroperm test

Figure 7: Acid saturation process

3.4 Key Milestone

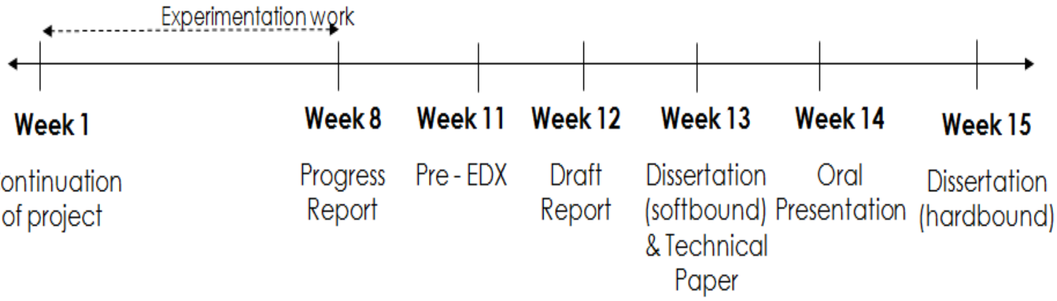
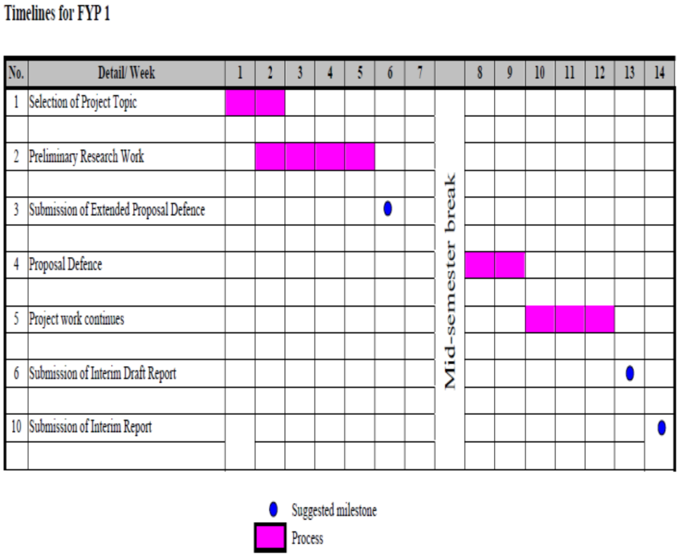


Figure 8: Key Milestone for Final Year Project-II

3.5 Project Gantt Chart

Below are the project Gantt chart for both semester of Final Year Project (FYP-I and FYP-II).

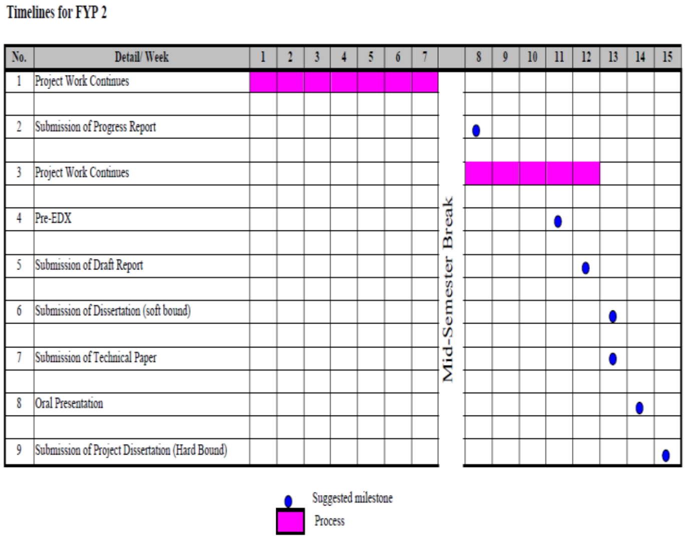


Timelines for FYP 1

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■						Mid-semester break							
2	Preliminary Research Work		■	■	■	■										
3	Submission of Extended Proposal Defence						●									
4	Proposal Defence									■	■					
5	Project work continues											■	■	■		
6	Submission of Interim Draft Report														●	
10	Submission of Interim Report															●

● Suggested milestone
■ Process

Figure 9: Gantt chart for Final Year Project-I



Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

● Suggested milestone
■ Process

Figure 10: Gantt chart for Final Year Project-II

CHAPTER 4

RESULT AND DISCUSSION

This experiment does not imply common acidizing treatment, since the cores are only saturated in acid, not injected. It also does not go through all stages of acidizing process i.e. *pre-flush*, *main treatment*, and *post-flush*. As mentioned before, the main function of matrix acidizing in sandstone formation is to remove or dissolve acid-removable damage or plugging in the perforations and in the formation pore network near the wellbore[8]. Permeability and skin factor are the major aspects to be considered before and after the stimulation. Minerals and fines migration can occur during well operations, but for this experiment the objective that will only be considered is to determine the correct acid concentration to increase the low permeability of the core samples.

The result for the first poroperm experiment (before acid saturation) is uncommon compared with normal sandstone core from the real formation. The author supposes that the mixture of sand grains and epoxy resin + hardener does not create a good pore spaces for the core. This can be seen from Scanning Electron Micrographs (SEM) figure later. Details reason is unknown but the author assumes that the resin reacts as cement and closes the connection between the pores. Also because the grain size of the cores is coarse, there are not many spaces to be occupied by fluids. Moreover, the cores are not prepared with formation temperature or pressure, which makes them more distinct with usual core sample taken from the wellbore. These are few reasons why the values for permeability and porosity are very small.

Table 4 shows acid concentration used for each sample and the result after acid saturation, which are significantly increased except for Sample-9 which was saturated in fluoboric (boric acid + HF).

Sample	HCl(%)	HF(%)	Δϕ (%)	Δk∞ (%)
1	12	3	-13.35	-13.39
2	12	5	86.67	409.09
3	**12**	**6**	**235.97**	**470.87**
4	12	8	172.03	582.05
5	15	3	15.33	74.32
6	**15**	**5**	**17.06**	**603.37**
7	15	8	116.29	417.02
8	15	6	66.29	301.11
9	**Fluoboric Acid**	**-**	**-95.73**	**-22.73**
10	15	-	-57.68	23.15

Table 4: Acid concentration and perm-poro changes for each sample

From the result, the most increment for permeability is shown by Sample-6 (603.37%) which saturated in HCl 15% + HF 5%. Sample-3 increased the porosity the most (235.97%) and increases the permeability quite high (470.87%), saturated in HCl 12% + HF 6%. Fluoboric acid decreases both permeability (-22.73%) and porosity (-95.73%). **Figure 11** presents the graphical results of both permeability and porosity changes.

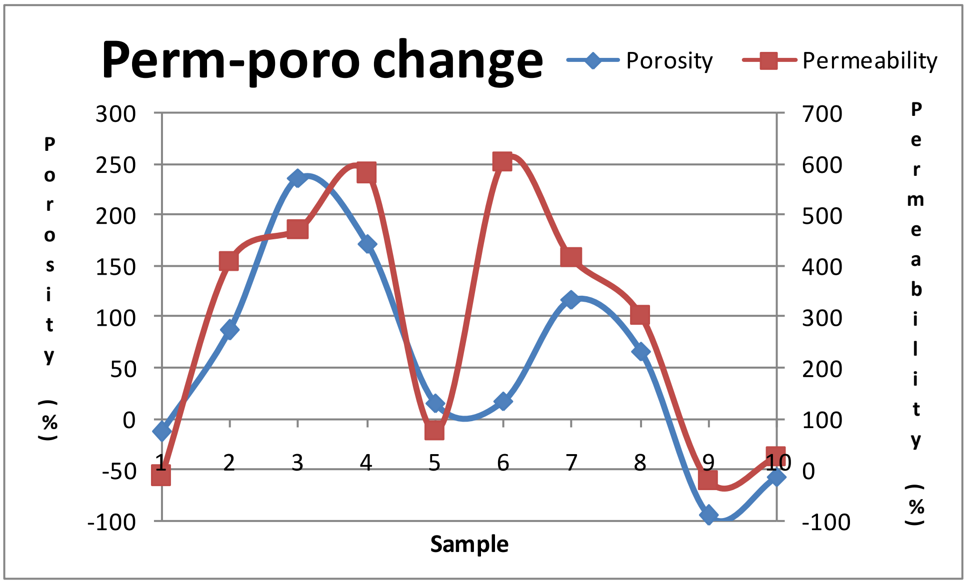


Figure 11: Permeability and Porosity changes

By observing the graph above, it appears that acids concentration is not necessarily proportional with permeability and porosity increment. For example, HCl 12% increase the porosity more than HCl 15% but not implied for the permeability. Sample-3 and Sample-4 shows higher permeability compare with Sample-7 and Sample-8 with the same concentration of HF. Yet, HF 8% does not yield the highest result although it is the highest concentration of HF used. The result indicates that the right amount and combination of acids used, *HCl + HF*, will result in optimum increment, not necessarily the amount of concentration only.

Furthermore, for this experiment, hydrochloric acid (HF) gives significant effect to the core. Based on the result, by saturating Sample-10 in a solution containing hydrochloric acid (HCl) only will not give a good result, as the porosity is decreasing (-57.68%) and the permeability is slightly increasing (23.15%). It can be concluded that this type of cores does require HF to increase their properties, both permeability and properties.

As mentioned earlier in the literature review, HF is the only acid that dissolves siliceous minerals significantly. The concentration of HF used normally does not exceed 3%, except under special circumstances e.g. conglomeratic sands, and other consolidated sands. Nevertheless, HF concentration can be increased up to 5%-10%. The only approach to prove the advantage of using a high-concentration HF mixture in a conventional procedure is through core flow testing, which in this experiment is being applied although not using the actual formation core of interest.

The problem with high-concentration of HF in combination with excess HCl is that the mixture will damage the the rock competency and lead to near-wellbore formation failure, sloughing in perforation thus to sand production.

Back to the formation characteristic itself, in certain cases, sandstone acidizing with high-concentration of HF can be successful and will not damage the formation until significant extent. History proved that by using HCl 12% + HF 10% created channels in sandstone formation in the Cook Inlet of Alaska in the late 1960s. From the experiment, the high-concentration HF created channels between grains, re-precipitation and fines migration can be overcome, as evidenced in core testing.

By considering and understanding the explanation above, the result for this project may be considered reasonable as the HF affects the permeability changes appreciably. The permeability increases quite high when high-concentration HF is used in the solution. Yet, this result can't be applied directly to similar or nearby formation because it is only done in atmospheric condition (pressure and temperature) and not in the real formation condition (high pressure and high temperature). Also, high-concentration of HF may lead to more formation damage. Thus, all considerations have to be taken into account before deciding the acids combination used.

F**igure 12** shows how Sample-6, which gives the highest increment for permeability, reacts with the acid combination. The color will turn more yellow when the acids react with the core.

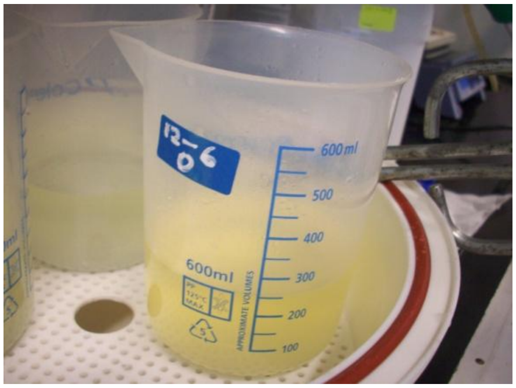


Figure 12: Sample-6 contains HCl 12% + HF 6%

Scanning Electron Micrographs (SEM) has been run to see the effect of permeability and porosity changes. From the result, SEM illustrates how the acid combinations whether opens or closes the pore spaces between the grains, depends on what combinations of acids used. For example, SEM for Sample-3 and Sample-6 prove that the acid mixtures used (HCl + HF) successfully increases the permeability and porosity by abundant pore spaces and channels in between the grains. The enlarged figure of SEM also shows that the combination of HCl + HF obliterate the sealed pore spaces thus creating channels, in contrast with fluoboric acid. SEM for Sample-9, saturated with fluoboric acid, shows the bonding between grains and epoxy resins + hardener doesn't break and create no pore space there. This is why the permeability and porosity decreases.

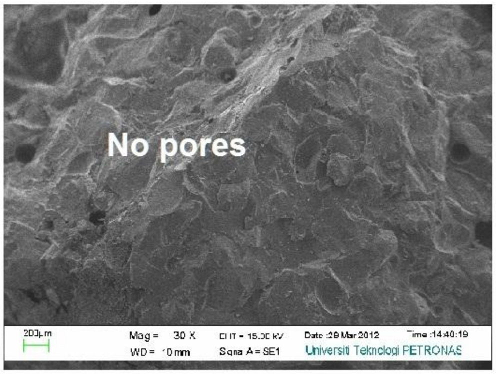


Figure 13: Sample-6 before acid saturation

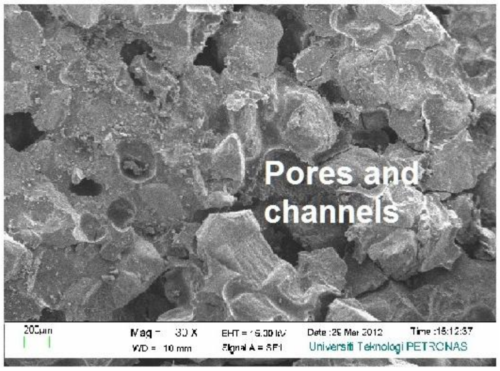


Figure 14: Sample-6 after acid saturation

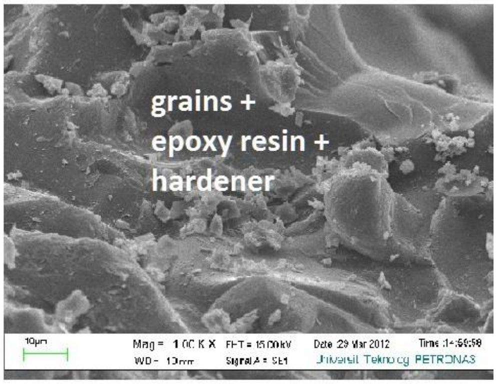


Figure 15: Sample-9before acid saturation

Figure 16: Sample-9 after acid saturation

CHAPTER 5

CONCLUSION and RECOMMENDATION

5.1 Conclusion

In sandstone formation, matrix acidizing treatment should be designed primarily to remove or dissolve acid-removable damage or plugging in the perforations and in the formation pore network near the wellbore [8]. In this experiment, the acidizing treatment is used to increase rock properties, especially permeability, by saturating the core samples taken from Paka Beach, Terengganu, in various acid combinations with different concentrations. For this project, the author use and mix *Conventional acid systems* e.g. Hydrochloric (HCl) acid, Hydrofluoric (HF) acid, and the most common *Retarded hydrofluoric-based acid (RHF)* which is fluoboric acid. From the results, the highest permeability is obtained by saturating the core sample in a mixture of HCl 15% + HF 5%, whereby the highest increment for porosity is achieved by saturating the core with HCl 12% + HF 6%. On the other hand, fluoboric acid gives the lowest increment and decreases both permeability and porosity. Scanning Electron Micrographs (SEM) shows the proof of permeability and porosity increment or decrement from the figures attained.

By analyzing all results, permeability and porosity changes also the SEM figures, the author may conclude that the amount of acids used is not necessarily proportional with permeability increment. The proper combination and concentrations of acids will give higher increment based on acid solubility of the rock itself. Higher amount of acids does not always result in higher permeability. Also for this type of sample, HF is required in order to create channels in between the pores. Yet, it is important to be taken into account that the acids combination may not be suitable for the real formation as the experiment was not done at real formation condition, and the cores were only saturated in acids not injected.

In conclusion, conventional acid systems are proven to increase the permeability and porosity of the sample from sandstone formation.

5.2 Recommendation

After all work has been done and the author has come out with the result, there are few things to be considered for improvement regarding this project. After doing this project for two semesters, the author has obtained the importance and the effect of matrix acidizing. The main objective of this project is to determine the most suitable acid formulation for sandstone formation taken from Terengganu sand. It is recommended to prepare the sand sample in formation pressure and temperature, which can give more accurate data for permeability and porosity test. Furthermore, the author suggested UTP to provide machines or equipment that can be used for matrix acidizing. The tools would be very beneficial for more research that will be held later on for the university.

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APPENDICES

Table 1: Perm-poro data before acid saturation

Sample	Input			Vp (cc)	kair (md)	k∞ (md)	Vgrain (cc)	b (psi)	ϕ (%)	Vbulk (%)	ρgrain (cc)	ρbulk (gr/cc)
	d (mm)	L (mm)	Weight (gr)									
1	25.2	50.6	44.15	2.182	17.079	14.641	23.055	2.374	8.65	25.237	1.934	1.767
2	25.1	51.4	46.85	-2.441	0.064	0.044	27.874	6.704	-9.6	25.433	1.681	1.842
3	25.3	50.8	43.73	0.738	0.127	0.127	24.8	0	2.9	25.538	1.763	1.712
4	25.1	50.4	46.06	-1.275	0.043	0.078	26.214	-6.366	-5.113	24.938	1.757	1.847
5	25.1	51	45.9	-0.677	0.035	0.074	25.912	-7.571	-2.7	25.235	1.771	1.819
6	25.1	51	44.3	1.803	0.208	0.208	23.432	0	7.15	25.235	1.891	1.755
7	25.14	51.56	45.893	-2.233	0.107	0.094	27.827	2.003	-8.724	25.594	1.649	1.793
8	25.16	51.86	51.39	-2.233	0.128	0.09	28.006	5.94	-8.62	25.784	1.783	1.937
9	25.13	51.39	46.16	-1.169	0.126	0.132	26.658	-0.636	-4.586	25.489	1.732	1.811
10	25.16	51.68	48.935	-1.791	0.114	0.108	27.485	0.692	-6.931	25.694	1.78	1.905

Table 2: Perm-poro data after acid saturation

Sample	Input			Vp (cc)	kair (md)	k∞ (md)	Vgrain (cc)	b (psi)	ϕ (%)	Vbulk (%)	ρgrain (cc)	ρbulk (gr/cc)
	d (mm)	L (mm)	Weight (gr)									
1	25.2	50.6	44.49	1.891	14.887	12.681	23.346	2.48	7.495	25.237	1.906	1.763
2	25.1	51.4	46.158	-0.323	0.224	0.224	25.756	0	-1.27	25.433	1.792	1.815
3	25.3	50.8	43.261	2.488	0.826	0.725	23.05	1.984	9.743	25.538	1.877	1.694
4	25.1	50.8	45.453	0.926	0.532	0.532	24.211	0	3.683	25.136	1.795	1.729
5	25.1	51	45.73	-0.577	0.129	0.129	25.812	0	-2.286	25.235	1.772	1.812
6	25.1	51	44.198	2.112	1.567	1.463	23.123	1.02	8.37	25.235	1.911	1.751
7	25.14	51.56	45.314	0.364	0.486	0.486	25.23	0	1.421	25.594	1.796	1.771
8	25.16	52	49.501	-0.751	0.37	0.361	26.604	0.369	-2.906	25.853	1.861	1.915
9	25.13	51.39	46.089	-2.2899	0.102	0.102	27.777	0	-8.976	25.489	1.659	1.808
10	25.16	51.68	48.901	-2.808	0.127	0.133	28.502	-2.016	-10.929	25.694	1.716	1.903

Figure-1: Porosity values before and after acid saturation

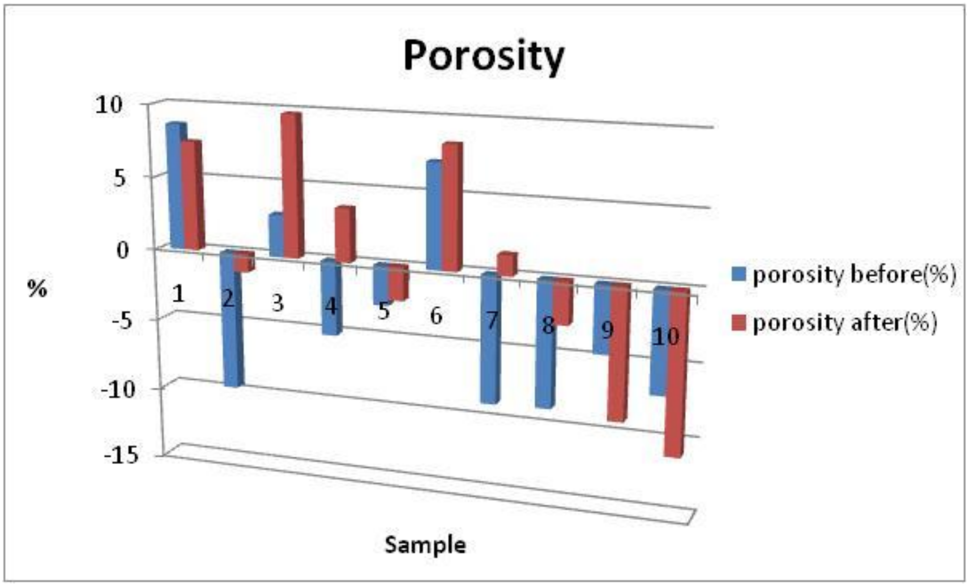


Figure-2: Permeability values before and after acid saturation

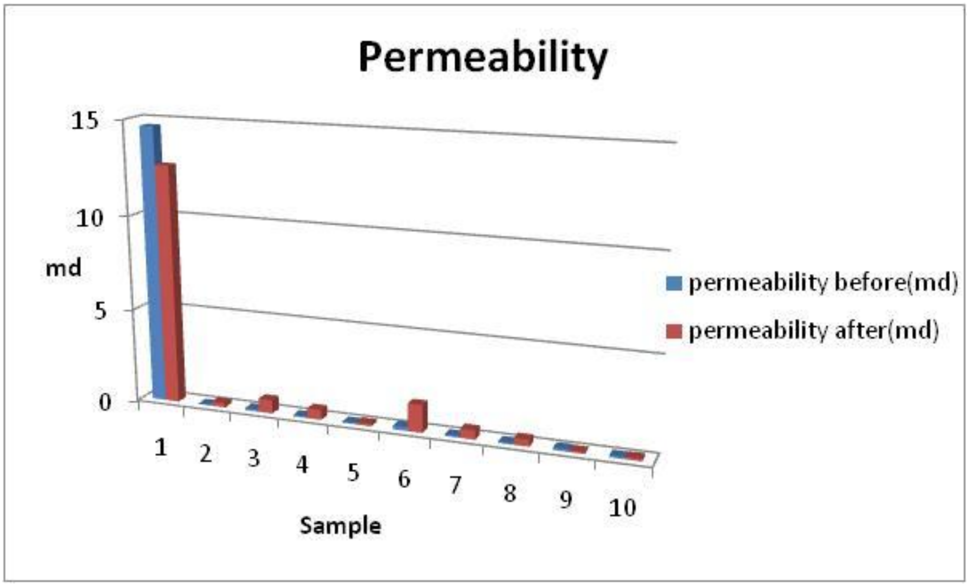


Figure-3: Sand preparation into core in PVC pipes

Figure-4: After the core is hardened and taken out from PVC pipes

Figure-5: The cores are cemented in a rectangle plastic container

Figure-6: The cores after being drilled to a size of 1.5” diameter and 2” long

Figure-7: VINCI Poroperm machine

Figure-8: Boric Acid

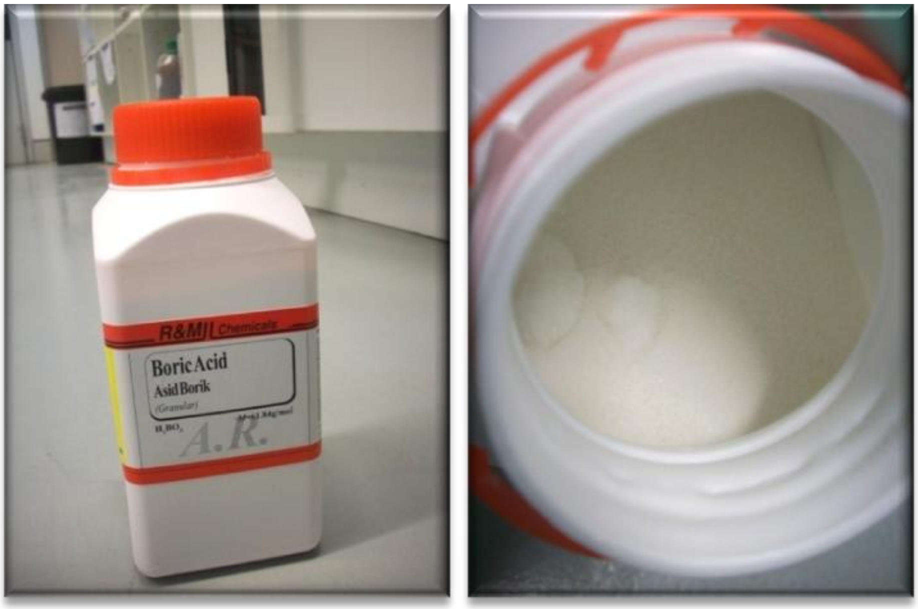


Figure-9: Boric Acid preparation in fume hood using warm water (50^{o}C)

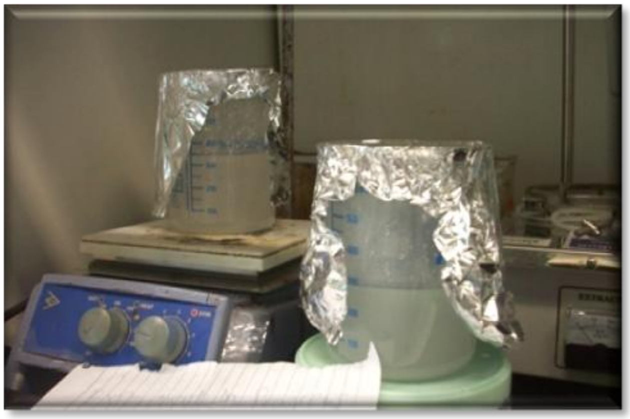
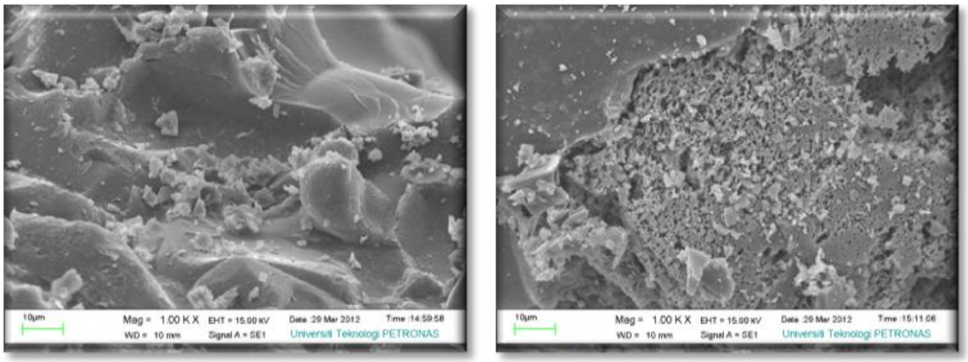


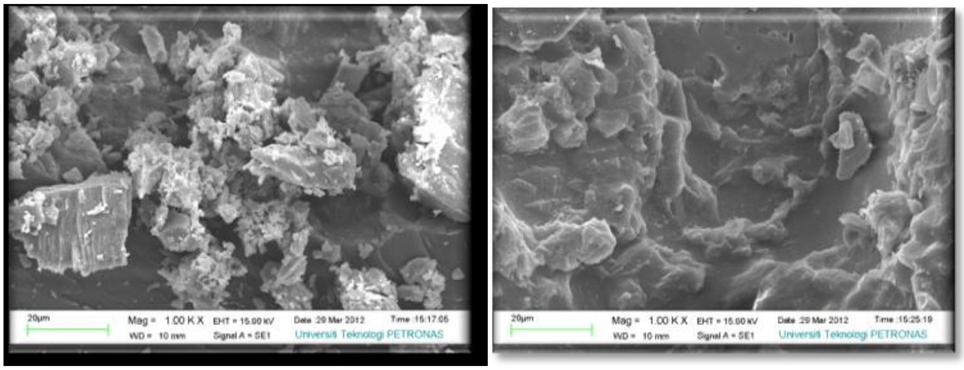
Figure-10: Acids used (HCl, HF, Boric Acid)

Figure-11: SEM picture for Sample-0, Sample-3, Sample-6, and Sample-9



Sample-0 (original sample)

Sample-3 (highest porosity)



Sample-6 (highest permeability)

Sample-9 (lowest porosity and permeability)

Appendix A
Example calculation:

- To make a solution of HCl 15% + HF 3% in 250ml total solution

Initial concentration of HCl : 37%
Initial concentration of HF : 48%
for all acids combinations, initial concentrations of HCl and HF are the same

HCl 15% → $M_1V_1 = M_2V_2$
→ $(37\%)(V_1) = (15\%)(250\text{mL})$
→ $V_1 = V_{HCl} = 101.35\text{mL}$

HF 3% → $M_1V_1 = M_2V_2$
→ $(48\%)(V_1) = (3\%)(250\text{mL})$
→ $V_1 = V_{HF} = 15.625\text{mL}$

Distilled water → (250-101.35-15.625)mL = 133.025 mL
~ For other acids combinations, the calculation is the same with different V_1 and M_2 values ~

- To make fluoboric acid in total of 250mL solution.

Fast Reaction:
$H_3BO_3 + 3HF \rightarrow HBF_3OH + 2H_2O$

Slow Reaction:
$HBF_3OH + HF \leftrightarrow HBF_4 + H_2O$

  - Boric acid is in solids form, with MW = 20.01gr/mol
  - mass = Molar x Volume x MW = (1) x (0.25L) x (20.01gr/mol)
    = 15.4575gr
  - mass of HF 3M = 31.2656gr; $\rho_{HF(48\%)} = 1.15$; Volume (HF 3M)
    = (mass/ρ)
    = 27.187mL
  - mass of HF 1M = 10.4218gr; Volume (HF 1M)
    = (mass/ρ)
    = 9.062mL
  - Volume (distilled water) = (250 – 27.187 – 9.062)mL = 213. 751mL

Steps:

1. Mix 3M of HF (27.187mL) with boric acid (15.4575gr H_3BO_3) together with distilled water required (213.751mL) using magnetic stirrer on hotplate, placed inside the fume hood.
2. Set the hotplate temperature to 50^{o}C, stir for one hour until the mixture blends and no solids can be seen.
3. Add 1M of HF (9.062mL) into the solution and stir again for one day (24hrs) with the same temperature.
4. Saturate the core for 4-hours like other samples.