STUDY OF ACID RESPONSE OF QATAR CARBONATE ROCKS

A Thesis

by

ZHAOHONG WANG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Petroleum Engineering

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Approved by:

Chair of Committee,	A. Dan Hill
Committee Members,	Ding Zhu
	Zhengdong Cheng
Head of Department,	Stephen A. Holditch

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ABSTRACT

Study of Acid Response of Qatar Carbonate Rocks. (December 2011)

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Chair of Advisory Committee: Dr. A.D.Hill

The Middle East has 62% of the world's proved conventional oil reserves; more than 70% of these reserves are in carbonate reservoirs. It also has 40% of the world's proved conventional gas reserves; 90% of these reserves are hold in carbonate reservoirs.

Recently papers published from industry discussed the techniques, planning, and optimization of acid stimulation for Qatar carbonate. To the best of author's knowledge, no study has focused on the acid reaction to Qatar carbonates. The lack of understanding of Qatar carbonate especially Middle East carbonates and the abundance of Middle East carbonate reservoirs is the main motivation behind this study.

This work is an experimental study to understand the acid response to Qatar rocks in rocks with two types: homogenous carbonate and heterogeneous carbonate. A large portion of this research is to further investigate the impact of centimeter scale heterogeneity on the acid stimulation using Qatar rocks. Qatar carbonates have multi-scale heterogeneities which may cause the impact of the injected acids to differ from homogenous case. Recent published field data indicate a much smaller number of pore volume to breakthrough compared with experimental measurement with homogeneous

carbonate and heterogeneity is believed to be one of the contributors of causing the low field measurements.

In this case, acid linear core-flood experiments were conducted with carbonate core samples of different petrophysical properties to study the impact of both separated and connected vugs and channels on pore volume to breakthrough. Computerized tomography was used in characterization of the heterogeneities. One experiment simulated the response of acid to heterogeneous carbonate in downhole condition with drill-in fluid damage.

Homogeneous rock was cored from a well in Qatar. The optimal injection rate was pursued through acid core flood experiments for acid stimulation design and for further reference.

It is been discovered that the optimum injection rate for heterogeneous carbonate exists. For the similar acid flux, the corresponding PV_{BT} for buggy limestone correlates inversely with the fraction of total porosity comprised by vugs. For vuggy carbonates with connected vugs and channels, whether or not formation damage exists, the acid tends to create new pore space nearby to the existing vugs and channels. Different strategies need to be made regarding acid stimulation design with homogeneous carbonate, heterogeneous carbonate with separated vugs and channels and heterogeneous carbonate with connected vugs and channels.

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DEDICATION

This work is dedicated to

My mother Yan Song

My father Xishuang Wang

& to Fei

ACKNOWLEDGMENTS

I would like to thank my committee chair, Dr. Hill, and my committee members, Dr. Zhu and Dr. Cheng, for their guidance and support throughout the course of this research.

Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience.

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CHAPTER I

INTRODUCTION

1.1 Statement of the Problem

Carbonate reservoirs play a quite important role in oil and gas reservoirs. More than 60% of the world's oil and 40% of the world's gas reserves are held in carbonates. The Middle East has 62% of the world's proved conventional oil reserves; more than 70% of these reserves are in carbonate reservoirs. It also has 40% of the world's proved conventional gas reserves; 90% of these reserves are hold in carbonate reservoirs.

Acid stimulation of carbonate reservoirs is a widely used conventional technique to increase the productivity of the wells. It is a process of injecting a fluid into the formation, below the fracturing pressure to create conductive channels to enhance permeability. The dissolution process occurs when carbonate reacts with acid and leads to wormhole penetration.

Recently papers published from industry discussed the acid stimulation regarding its techniques (Thabet et al, 2009), planning (Abou-Sayed et al, 2007), and optimization (Postl et al, 2009) for Qatar carbonate reservoirs. To the best to author's knowledge, no study has focused on the acid response of Qatar carbonates. The lack of understanding of Qatar carbonate and the abundance of Middle East carbonate reservoirs is the main motivation behind this study.

This thesis follows the style of *Society of Petroleum Engineering.*

Two types of rocks were used in this research to study acid response to rock: Maersk homogeneous carbonates core sample and Qatar outcrop heterogeneous carbonates. For Qatar heterogeneous carbonate, we focused on further investigation of the effect of heterogeneity on the acid response to rock based on previous research.

Previously, The effect of carbonate heterogeneity on acid stimulation were studied under three scales: Pore scale, millimeter to centimeter scale and reservoir scale (Thabet et al, 2009) .To the best of author's knowledge, for the effect of pore scale heterogeneity on acid stimulation, the only published result was done by Ziauddin and Bize (2007). For the effect of millimeter to centimeter scales\ heterogeneity on acid stimulation, Izgec and Keys (2008) conducted the only experimental and modeling study. For Reservoir scale, a few papers have been published, mainly focusing on vertical permeability heterogeneity in thick carbonate reservoirs (Thabet et al, 2009).

Even though previous research has studied on millimeter to centimeter scale heterogeneity, it has not been fully investigated due to the complex nature of vuggy carbonates. Homogeneous carbonate study was done using cores from a Qatar well which the crude oil from the oil zone sealed in the core, and the fluid we used to saturate the core is identical to the formation fluid. These experimental conditions are the closest approaching to the downhole condition in Qatar wells, The results of optimal acid injection rate measured in the lab should be the most accurate observation of the optimal acid pumping rate for Qatar wells, and the results from this study can be applied as further reference to Qatar wells with similar rock/fluid properties and downhole condition.

1.2 Background and Literature Review

It is necessary to understand the fundamental theory of the acid response to rock. The reaction for HCl with calcite is:

$2HCl + CaCO_3 \Leftrightarrow CaCl_2 + H_2O + CO_2$

For dolomite the reaction is:

$4HCl + CA\ Mg\ (CO_3)_2 \Leftrightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2$

The acid reacts differently to rock corresponding to the acid injection rate .There are four modes of acid attack, compact dissolution, diffusion-limited wormholing, fluid loss-limited wormholing, and uniform dissolution. At very low injection rates, the inlet face of the rock will be slowly consumed as acid diffuses to the surface, it is named compact dissolution. At relatively low injection rates, diffusion-limited wormholing is going to occur, which means that the volume of acid needed to propagate the wormhole a given distance decreases as injection rate decreases. At relatively high flow rates, the fluid loss is dominant due to the increasing of wormhole branches, yielding fluid loss-limited. At very high injection rates, uniform dissolution happens, the overall reaction rate become surface reaction-limited. The optimal injection rate exists between the relatively low flow rates and relative high flow rates, which requires the least amount of acid to penetrate a given distance (Petroleum Production Book, 1994).

Fig.1.1 shows the relationship of acid injection rate and volume of acid needed to breakthrough. It is observed that as acid injection rate increases, the volume of acid need to breakthrough decreases. The optimal injection rate can be reached, after that the acid volume needed to breakthrough increases as the injection rate increases.

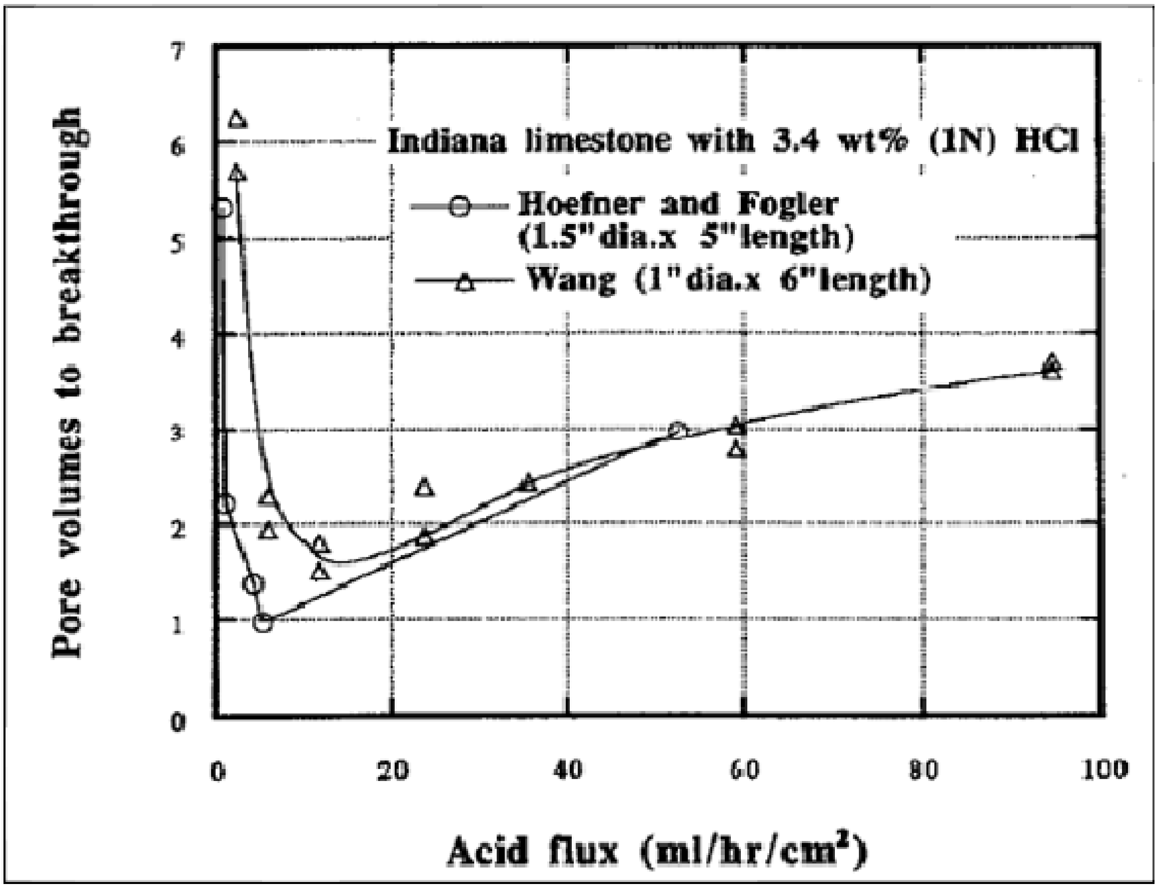

Fig. 1.1—Optimal Injection Rate (Wang, 1993)

Fig.1.2 represents the pattern of the wormhole in different acid injection rates. McDuff et al. (2010) conducted several experiments and use high-energy CT scanning services. The top portion is the conical wormhole pattern which results for the acidizing experiment performed at relatively low injection rates. The middle portion is the wormhole pattern which the acid injection rate is close to the optimal injection rate. The lower portion is the wormhole pattern in which the acid experiment was conducted at relatively high acid injection rate. As the acid injection rate increases above the optimal injection rate, it will form more branches.

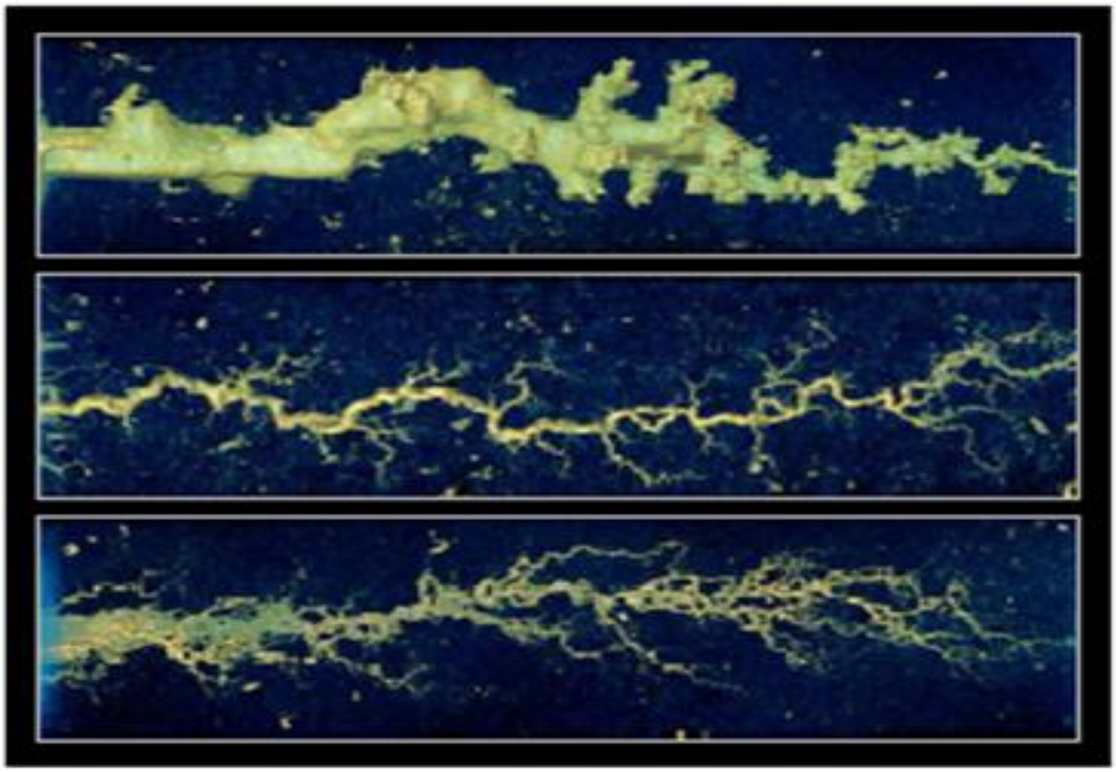

Fig. 1.2—Wormhole Pattern under Different Modes of Attack (McDuff et al, 2010)

Both experimental and theoretical studies have been performed for better understanding of the carbonate acid stimulation process. Williams et al. (1979) recommend maximum injection rate to avoid facial dissolution. Daccord (1987) and Daccord (1993) performed experiments by injecting water in the plaster in order to study the dissolution pattern with various injection rates.

A series of experiments was conducted by Wang et al. (1993) to pursue optimal injection rate under different experimental conditions to study the impact of rock mineralogy, temperature and acid concentration by injecting HCl. Fredd and Fogler (1998) conducted experiments using different acids to study the impact of reaction and transport mechanisms on wormhole growth. Bazin (2001) conducted similar experiment to the one conducted by Wang et al. (1993). All the experiments presented above were conducted using homogenous rocks in homogeneous cases.

To study the heterogeneity of carbonates, Ziauddin and Bize (2007) studied the effect of pore-scale heterogeneities on carbonate stimulation treatments by using Nuclear Magnetic Resonance (NMR), Computed Tomography (CT) and Scanning Election Microscopy (SEM) techniques. The results of the tests proved that the response of the carbonate to acid highly depends on the porosity spatial distribution.

Izgec and Keys (2008) presented both experiment and modeling work. Methodology to characterize the carbonate core was performed and a 3-D finite difference numerical model was developed based on Darcy-Brinkman formula. The results demonstrate that acid injection volume to breakthrough is affected by spatial distribution and connectivity of vuggy pore space.

In order to apply optimal injection rate to field conditions, Glasbergen et al. (2009) stated his rules of thumb. He recommended that to consider applying the optimal injection rate for HCl in limestone, it must be a higher-permeable formation. The reservoir pressure should be fairly uniform; the total zone height should be relatively short, less than 50 ft. When downhole condition is more complex than this, he stated "Using the more conservative result, which is highest injection rate, is then advised. Keep in mind that overshooting the optimum injection rate is always better than pumping at too low a flow rate."

Furui et al. (2010) presents a new model based on Buijse and Glasbergen's (2005) empirical wormhole model. The wormhole tip velocity was discovered to be higher for larger diameter cores and it explained why the apparent wormholing efficiency is greater for larger diameter core samples. **Fig.1.3** shows the skin value after carbonate matrix acidizing treatment of approximate 400 wells. The average skin value is -4 which indicates the average wormhole penetration distance can be 10 to 20 ft at least. Field-measured PV_{BT}=0.047 was 30% porosity rock.

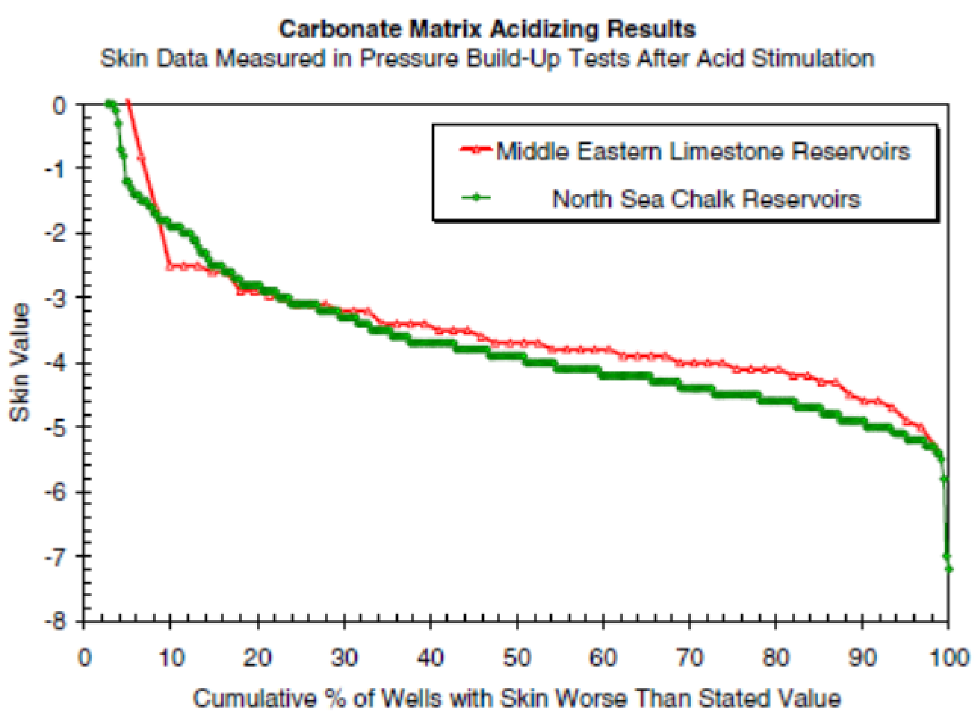

Fig. 1.3—Carbonate Matrix Acidizing Results from Field Data

1.3 Objectives of Research

The objective of this research is to understand the acid response to homogeneous and heterogeneous rocks from Qatar.

For heterogeneous rocks, the purpose is to further investigate the effect of millimeter to centimeter scale heterogeneity on acid stimulation. Izgec and Keys (2008) focused their experimental work on carbonates of which the vuggy pore space fraction is from 7% to 23% using 4 inch diameter and 20 inch length cores, and the vugs and channel are separated in these cores. In other words, Izgec and Keys (2008) study the effect of separated vugs and channels on relatively less vuggy carbonate on acid stimulation using 4 inch diameter cores.

We cannot tell whether or not optimum injection rate exists from Omer and Ryan (2008)'s data, the range of acid flux in this research is wider than Omer and Ryan (2008)'s data, which means the relationship of pore volume to breakthough and acid flux can be demonstrated more clearly. To know whether or not optimum injection rate exists in heterogeneous rock with separated vugs is one of the main objectives in this research. Previous homogeneous acidizing experiments were mainly using 1 inch diameter by 6 inch cores. The precise conversion of pore volume to breakthrough between 1 inch core and 4 inch core has not been discovered in vuggy carbonate, so that the comparison of pore volume to breakthrough between heterogeneous carbonate and previous homogeneous carbonate can only be roughly made from Izgec and Key's data.

In order to fully compare the vuggy carbonate breakthrough pore volume with homogeneous carbonate, the same core size is needed. One series of experiment has been done in 1 inch diameter and 6 inch length using Qatar outcrop to meet this requirement. A precise comparison can be made using the result from this work and previous homogeneous work.

For the fact that the characteristics of the connected vugs and channels cannot be fully represented by 1 inch diameter and 6 inch length cores, we used larger diameter core to understand the effect of connected vugs and channels on acid stimulation.

One experiment was done in order to understand how drill-in fluid behaves in these connected vugs and channels and how the acid stimulation responses to this buggy carbonate with drill-in fluid damage. For homogenous core sample from Qatar, a series of acid experiments were done in order to find out the optimal acid injection rate.

CHAPTER II

EXPERIMENTAL PROCEDURE

2.1 Experimental Conditions

Three series of experiments were conducted to study the acid response to rock. Heterogeneous carbonate rocks from a Qatar outcrop were cut to 1 inch diameter and 6 inch length cores and 4 inch diameter by 18 inch length cores. acidizing experiment was conducted using 1 inch diameter and 6 inch length cores at room temperature , with 300 psi overburden pressure and 1000 psi back pressure. We used fresh water to saturate the cores and 15 percent HCl to acidize the cores.

Two experiments were conducted with 4 inch diameter 18 inch length cores. One experiment was conducted at the same experimental condition as 1 inch diameter and 6 inch length cores. For the other experiment, water-based drilling mud was used to simulate the downhole condition with drill in fluid damage. **Table 2.1** lists the chemical components in the drilling mud. 50 psi overbalance pressure was applied on the inlet of the core in order to make the drilling mud flow into the connected vugs and channels. Homogeneous carbonate cores are approximately 1.5 inch diameter and 2.5 inch length with reservoir oil and water remain.

TABLE 2.1 DRILL-IN FLUIDS COMPOSITON (ZHANG, 2009)

Name	Product Name	Quantity per bbl		Quantity per gal				8 gal mud	
Water	Water	0.9	bbl	0.9	gal	0.9	gal	7.2	gal
Biopolymer	Xanthan Gum polymer	1.5	lb	0.0357	lb	16.2	g	129.6	g
KCl	Potassium Chloride	10.8	lb	0.2571	lb	116.6	g	933.1	g
NaCl	Salt	32.3	lb	0.7690	lb	348.8	g	2790.7	g
Organophilic Starch	Thrutrol	10	lb	0.2381	lb	108.0	g	864.0	g
Organophilic Carbonate	Thrucarb	6	lb	0.1429	lb	64.8	g	518.4	g
Sized CaCO3	Safe-Carb 10	24	lb	0.5714	lb	259.2	g	2073.6	g
Rev Dust	Rev Dust	20	lb	0.4762	lb	216.0	g	1728.0	g
pH Buffer	Caustic Potash	0.5	lb	0.0119	lb	5.4	g	43.2	g
Biocide	Myacide	0.25	lb	0.0060	lb	2.7	g	21.6	g

We use 25,000 ppm brine water to saturate in order to simulate the formation fluid and 15 percent HCl to acidize the cores at room temperature. **Table 2.2** shows the experimental condition summary in this research.

TABLE 2.2 EXPERIMENTS CONDUCTED IN THIS RESERCH

Sample Name	Size(inches)	Number of Experiments	Experiment condition		
			Temperature	Saturation	Acid Type
Qatar Outcrop	1 Diameter 6 Length	10	Room T	Fresh Water Saturated	15% HCl
Qatar Outcrop	4 Diameter 18 Length	2	Room T	Fresh Water Saturated	15% HCl
Core Plugs	1.5 Diameter 2.5 Length	7	Room T	25,000ppm Brine Saturated	15% HCl

2.2 Computerized Tomography

Computerized Tomography (CT) technique was applied to acidizing core flood experiment to study the wormhole pattern and to calculate the vuggy porosity fraction. **Fig.2.1** shows one slices of CT scan, which indicates the density information of the cross-sectional area at certain index of the core. The white color indicate the carbonate matrix, the black color outside the core indicate background. The black color portion in the carbonate matrix indicates vugs. Normally, for 1 inches diameter 6 inches long cores, it takes 105 slides to scan the entire core with 1.5 indexes. 3-D CT-Scan images were constructed by compiling all the cross-sectional slices. Vugs, channels and wormhole pattern can be observed from 3-D CT-Scan images.

Comparison of pre-scan and post-scan images is needed to better understand the acid behavior. **Fig. 2.2** shows the CT number of one slices of CT scan in excel. Each dot indicates one CT-number which ranges from -999 to around 3500.

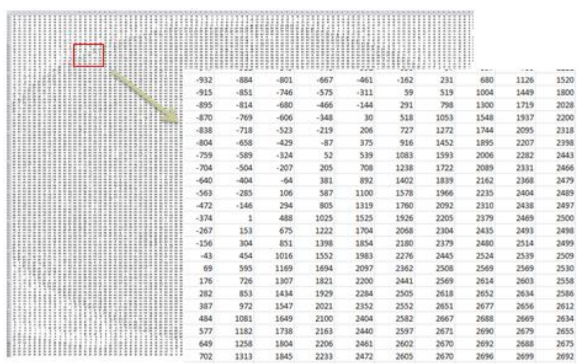

Fig. 2.1—Single Slice of CT-Scan

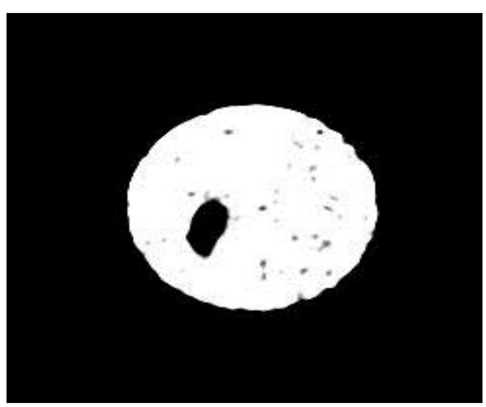

Fig. 2.2—CT Number Schematic in a Slide

CT number helps us to identify vugs from matrix. It represents the density of the object. Higher CT number represents objects with higher density while lower CT number represents objects with lower density**. Fig. 2.3** shows the CT-Scanner used in this study.

Fig. 2.3—Computerized Tomography Scanner

2.3 Pre-Experiment Preparation

One trip was made to Qatar to collect the outcrop rock block. **Fig. 2.4** shows the carbonate outcrop where the block of the rock comes. The whole block was shipped from Qatar to Texas A&M University Petroleum Engineering department (**Fig. 2.5**). Once the block arrived, pre-experiment preparation was needed.

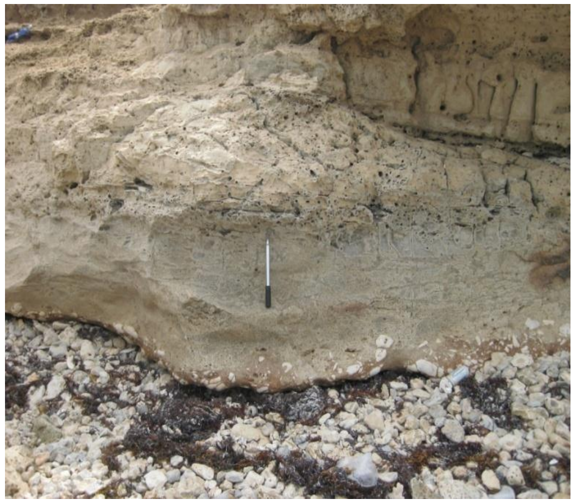

Fig. 2.4—Carbonate Outcrop

Fig. 2.5—Qatar Outcrop Block

2.3.1 Coring

The coring tools cut the rock to be cylinder with different diameter and various lengths. Qatar heterogeneous rock was cut to be 1 inch diameter with 6 inch length and 4 inch diameter with 18 inch length (**Fig. 2.6**).

Fig. 2.6—Homogenous Core before Acidizing Experiment

Homogeneous cores were sealed carefully and wrapped with plastics by the company in order to keep the original components in the core. They were cored to be 1.5 inch diameter and 2.5 inch long before shipping to us. **Fig.2.7** shows the cores before acidizing experiment.

Fig. 2.7—Qatar Outcrop Cores

2.3.2 Saturation

In order to conduct experiments under single-phase flow (water) or two-phase flow (water-oil) condition, saturating the core is needed. It is done by removing the air in the pore space and replacing it with liquid. The liquid used to saturate the core should be corresponding to the we pump before acidizing, normally we use fresh water or brine. This step needs to be done carefully to make sure all the air comes out of the matrix. Otherwise, the residual air will be compressed during the experiment and the permeability measurement will be difficult. Cores need to be under suction pressure provided by vacuum pump for 12 hours before conducting acidizing experiment. The Qatar outcrop cores were saturated with fresh water and the trial plugs were saturated with 25,000 ppm brine.

2.3.3 Refilling the Syringe Pumps

The volume of hydraulic oil in the syringe pumps should be higher than the sum of the volumes of water and oil needed in one experiment. Because the acidizing system cannot be open to air during the experiment ,the Syringe pump must be refilled before the experiment. For 4 inch diameter and 18 inch long cores, 1 L hydraulic oil is needed for one acidizing experiment while for 1 inch diameter and 6 inch cores at least 500 mL is needed.

Opening the inlet valve which connects to the container of hydraulic oil and closing the outlet valve which connects to the other part of the system and then pressing the "Refill" button can start the refill process. We observed that the pumps will suck not only oil but an amount of air in to its container. Any air remains will be pump in to the system, and it will leads to the unstable of the pressure and the measurement because of the air compression. In order to get rid of the air, wait for a while to make sure all the air goes to the top of the container in the pump after the first refill. After that, close the inlet valve and open the outlet valve. Press 'Run' and wait for all the air comes out. Repeat this step for several times to make sure there is no air in the syringe pump.

2.3.4 Refilling the Water and Acid Accumulator

The water and acid accumulators need to be refilled before the experiment. The water and acid share part of the flow line. It is important to ensure there is no acid remaining in the flow line before starting to refill the water accumulator and before starting the experiment. In order to achieve these, it is better to refill the water accumulator before refilling the acid accumulator, so that no acid will goes to the water accumulator and when the water and acid refilling is done, we can pump water into the flow line to get rid of the remain acid.

For homogenous core experiments, we used 25,000 ppm brine as the saturation fluid and injection fluid. In 1000mL of fresh water, 24.97 gram NaCl was mixed in to achieve this amount of brine.

The previous acid experiments normally use 15wt. % HCl. For this research, in order to compare the results with previous under the same condition, the acid concentration was 15% HCl. The commercial concentration ranges from 30% to 35% and acid dilution is needed to achieve the desired concentration.

In order to make 500mL of 15% HCl, 214mL of the commercial concentration of 35% HCl should be used and mixed with 286mL of fresh water. (Ryan’s dissertation)

After refilling water and acid accumulators, there are steps that need to be done before start pumping.

2.3.5 Check Flow Lines

It is quite common to see corrosion of flow line in these experiment where we need to use strong acid and It is necessary to check the flow line if there is any leakage before starting the experiment and fix those leakage. Normally, these leakages are not easy to find at atmospheric pressure. Connect inlet of the flow line to the core holder and outlet of the flow line to the core holder. Set the back pressure regulator to 500 psi and pump water into the flow line to check if there is leakage. If so, replace the corroded flow line and check again.

2.3.6 Place the Core and Connect the Flow Line

The flow line should be connected to the core holder as shown in **Fig.2.8** It is important to emphasize that there should be no air inside the core holder and also the flow line once we finish connecting the entire flow to the core holder. In order to achieve this, pump water through the flow line to replace all the air in the flow line and wait until the last minute to take the core out of the saturation fluid and place in the core holder to have the minimum loss of saturation fluid.

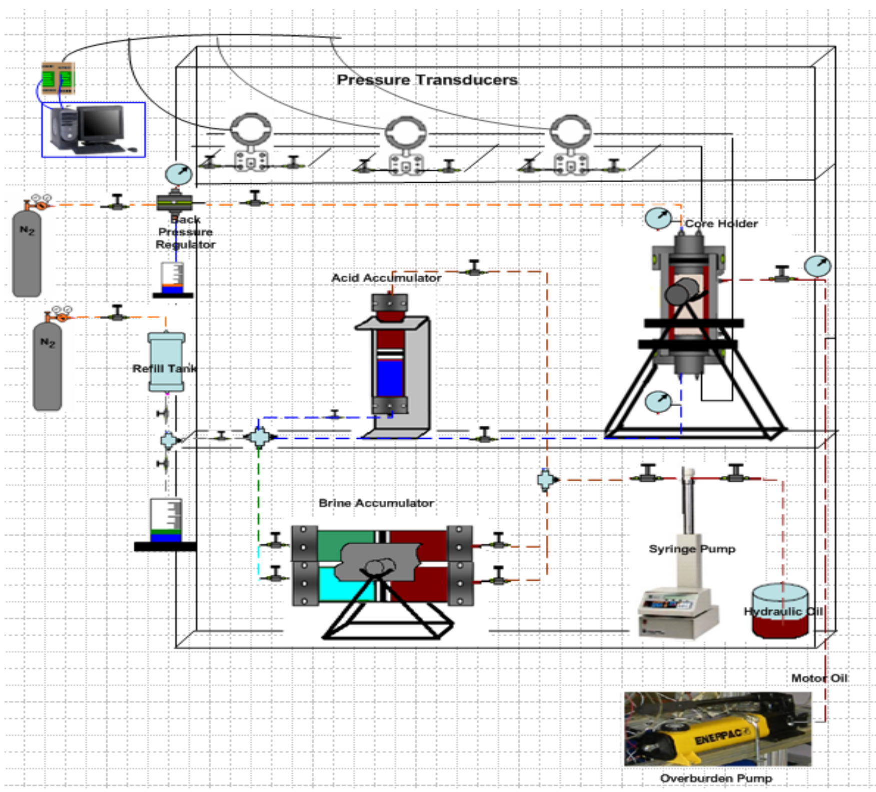

Fig. 2.8—Experiment Schematic

2.3.7 Applying Backpressure and Confining Pressure

The production of CO_2 will lead to the increase of pressure drop when acid react with calcite. In order to solve this problem as well as simulate the downhole condition. It is important to apply backpressure. For this study, 1000 psi was applied. The confining pressure can keep the acid flow inside the core. Normally, we need to apply at least 300 psi (confining pressure) higher than the inlet pressure. It was observed less sufficient overburden pressure could lead to the acid flow on the edge of the core and the wormhole shape is abnormal. A simple calculation can demonstrate the relationship:

Back pressure + Pressure drop = Inlet pressure

Inlet pressure + Confining pressure = overburden pressure

2.4 Apparatus Description

2.4.1 Core Holders

Three sizes core holder have been used in these experiments. They are:

1 inch diameter and 6 inch length core holder

1.5 inch diameter and 6 inch length core holder

4 inch diameter and 20 inch length core holder

Because the size of the trial plugs is 1.5 x 2.5 inch, the 1.5 x 3.5 inch spacer needed to be made in order to fit the 1.5x 6 inch length core holder. The 4 x 20 inch would fit the cores which length ranges from 18 inch to 20 inch, so that it was not necessary to make spacers for the 4 x 18 inch Qatar outcrop cores.

2.4.2 Spacers

The spacer can be made by waste core samples. The homogeneous limestone needs to be cut to meet the requirement of the sizes. It is important to drill several channels along the core so that the pressure drop when fluid passes the spacer is small and can be neglected in the acidizing experiment.

Fig.2.9 shows the water accumulator and refilling tank. The water accumulator is 4 L and the refilling tank is 2 L.

Fig. 2.9—Water Accumulator and Refilling Tank

Fig.2.10 shows the pressure transducer, which is used to measure, the pressure drop along the core.

Fig. 2.10—Pressure Transducer

Fig.2.11 shows the backpressure regulator, which provides the constant back pressure.

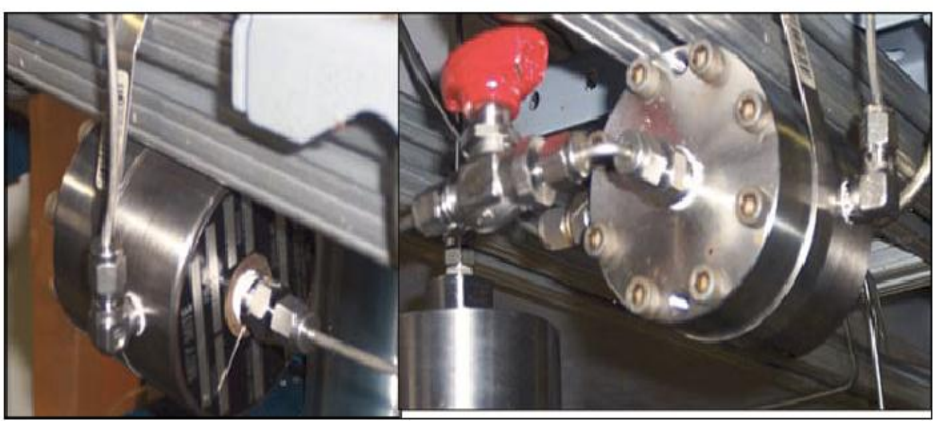

Fig. 2.11—Backpressure Regulator

2.5 Experimental Operation

2.5.1 Permeability Determination

The permeability of the core can be calculated using Darcy's law by measuring the pressure drop from the inlet and outlet to the core under the steady-state flow condition. No air should remain in any of the lines especially in the inlet and outlet of the pressure transducer lines in order to measure permeability accurately. The pressure drop should be measured between 20 psi and 1000 psi by changing the flow rate Keep the water flow line open and close the acid flow line by closing the related valves and then start the pump with a constant flow rate. Once the pressure reading does not change on the pressure transducer for a certain time, the pressure can be recorded to calculate the permeability. To check the pressure reading, we can calculate the difference from the reading of the inlet of the pressure gauge and the reading of the backpressure regulator, and compare the difference with the pressure reading the pressure gauge along the core to see if they are identical.

2.5.2 Acid Injection

Acid injection can be done by changing from the water flow line to acid flow line. The pump can be shut down for a short period of time for opening valves on the acid line and closely valve on the water line. The pressure drop will eventually drop from the steady-state pressure to below 15 psi and that indicates the acid has broken through the core. Acid injection rate and time need to be recorded for further calculation.

2.6 Post Experiment Procedures

1. After acid breakthrough the core, water needs to be pumped into the core to clean the acid remaining. Stop the pump, change from acid flow line to water flow line and start to pump at a higher injection rate.

2. Relieve the backpressure pressure.

3. Remove the flow line from inlet and outlet of the core holder.

4. Remove the overburden pressure.

5. Take apart the core holder and carefully take the core out. This step must be done carefully to avoid breaking the core, especially in these vuggy carbonate experiments.

6. Displace the acid out of the acid accumulator and refill water to the acid accumulator to prevent acid accumulator corrosion.

7. Clean up the core holder and the rest of the apparatus.

CHAPTER III

RESULTS AND ANALYSIS

3.1 Results and Analysis of Homogeneous Cores

We keep experimental conditions similar to the reservoir condition by saturating with 25,000 ppm brine, and keep crude oil inside the cores while conducting acidizing experiments. **Appendix A** shows the pressure drop along the core and all the measured data. **Appendix B** shows the pictures of the inlet and outlet before and after the experiments. **Appendix C** shows the CT-Scan Images before and after the acidizing experiment. From the CT-Scan Images before the acidizing experiment, it is easy to tell the core is homogeneous. The variation of color is due to the crude oil in place. The lighter color on the CT-scan images after acidizing indicates the wormhole position.

Table 3.1 shows the permeability is ranging from 0.33 to 1.3 mD. Porosity is ranging from 0.15 to 0.23. All the experiments were conducted in order to understand the relationship between the acid injection rates and the pore volume to breakthrough. We realize that even with crude oil in place, the acid flux still affects the acid response to rock.

The acid flux is calculated using the following equation.

$$V_i = \frac{q}{A\phi} \quad \text{(3.1)}$$

V_i is the acid flux (interstitial velocity), q is the acid injection rate, ϕ is the porosity of the core. A is the cross-sectional area.

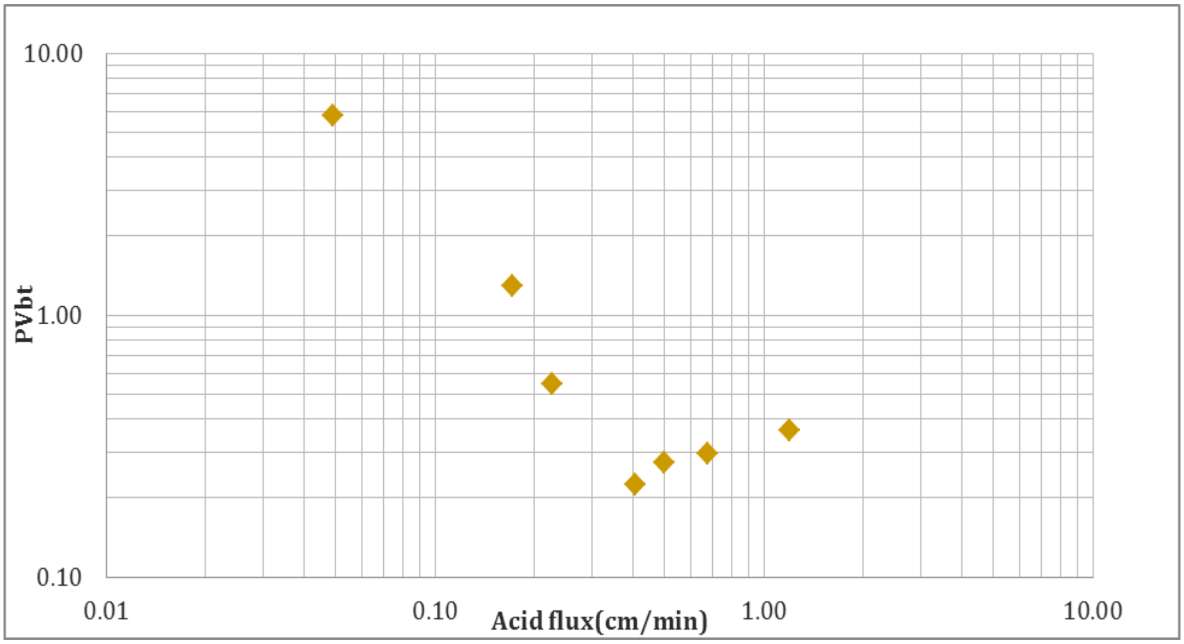

Fig. 3.1—Optimal Injection Rate Curve for Homogenous Cores

A relatively accurate optimum injection rate can is achieved which is shown in **Fig 3.1**. The pore volume to breakthrough number decreases rapidly as acid injection rate increases below the optimal injection rate, and then it increases slightly above the optimal injection rate as the acid injection rate increases. From observation of the shape of the curve and the pictures from inlet and outlet after acidizing. It is clear that mainly two modes of acid attack dominated in these experiments: diffusion-limited wormholing and fluid loss-limited wormholing. The optimal acid flux was found to be 0.41 cm/min and optimal pore volume to break through number is 0.23 accordingly between these two modes of acid attack.

TABLE 3.1—PROPERTY DATA FOR EACH CORE SAMPLE

No.	Porosity	Water in.	Acid Injection Rate (cc/m)	Permeability (mD)	Acid. T (m)	PV_{BT}	Acid Flux (cm/min)
2	0.20	0.50	0.50	0.72	21.50	0.55	0.23
3	0.15	0.25	0.25	0.63	61.00	1.29	0.17
5	0.19	0.10	0.10	0.97	793.00	5.76	0.05
8	0.23	1.00	1.00	1.09	6.17	0.23	0.41
9	0.21	1.15	1.15	0.98	4.20	0.27	0.50
11	0.20	1.50	1.50	0.33	4.65	0.29	0.67
12	0.20	2.50	2.50	1.30	3.15	0.36	1.20

3.2 Results and Analysis of Qatar Heterogeneous Carbonates

3.2.1 Geological Description

The nature of heterogeneous rock is complex and geological classification can be used to describe the rock since the rock structure will affect acid response.

Dunham classification (1962) is based on the mud to grain ratios and the arrangement of framework grains. Dunham classification (**Fig.3.2**) works well for detrital carbonates but it cannot describe textures or fabrics. For this study, Qatar outcrop falls in the category of grainstone. The original components are not bound together during deposition. It is lack of mud and is grain-supported. It has some moderate digenetic dissolution which makes it “chalky” in appearance.

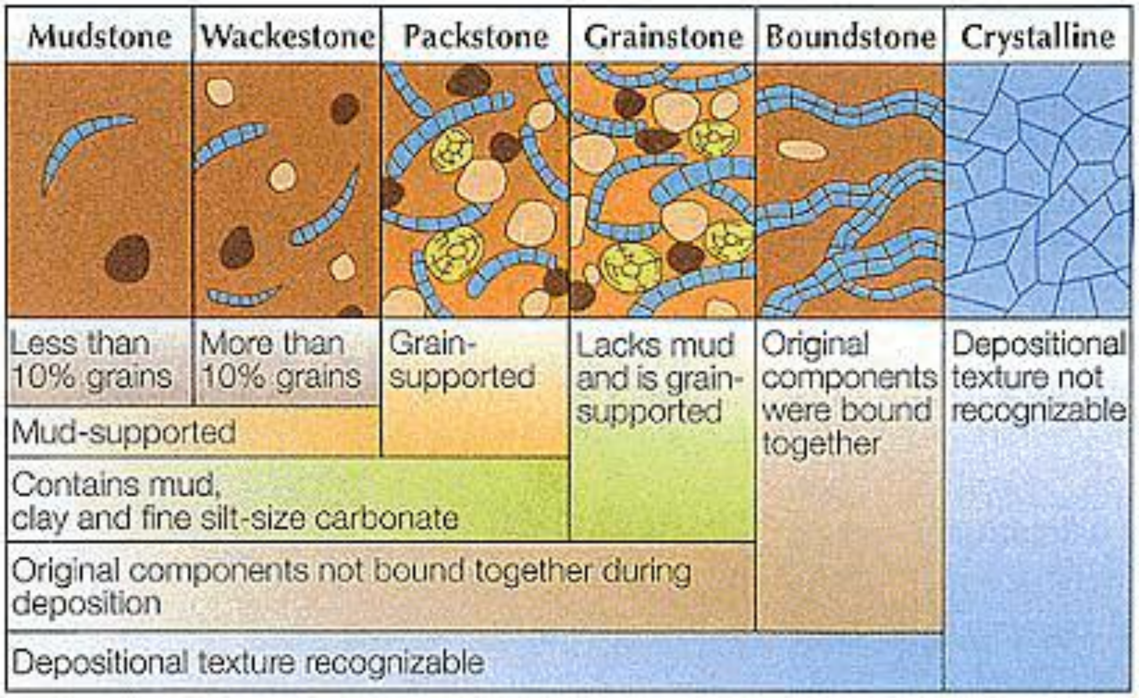

Fig. 3.2—Dunham Classification (1962)

In order to describe textures and fabrics, Choquette and Pray (1970) classify carbonate porosity focusing on incorporating time and mode of origin. They organized different pore types into three categories: fabric selective, not fabric selective, fabric selective or not. Fabric refers to the spatial arrangement and orientation of the grains in sedimentary rocks. Fabric selective means the porosity conforms to the spatial arrangement and orientation of the grains in sedimentary rocks. **Fig 3.3** is the essential elements of the Choquette-Pray (1970) porosity classification.

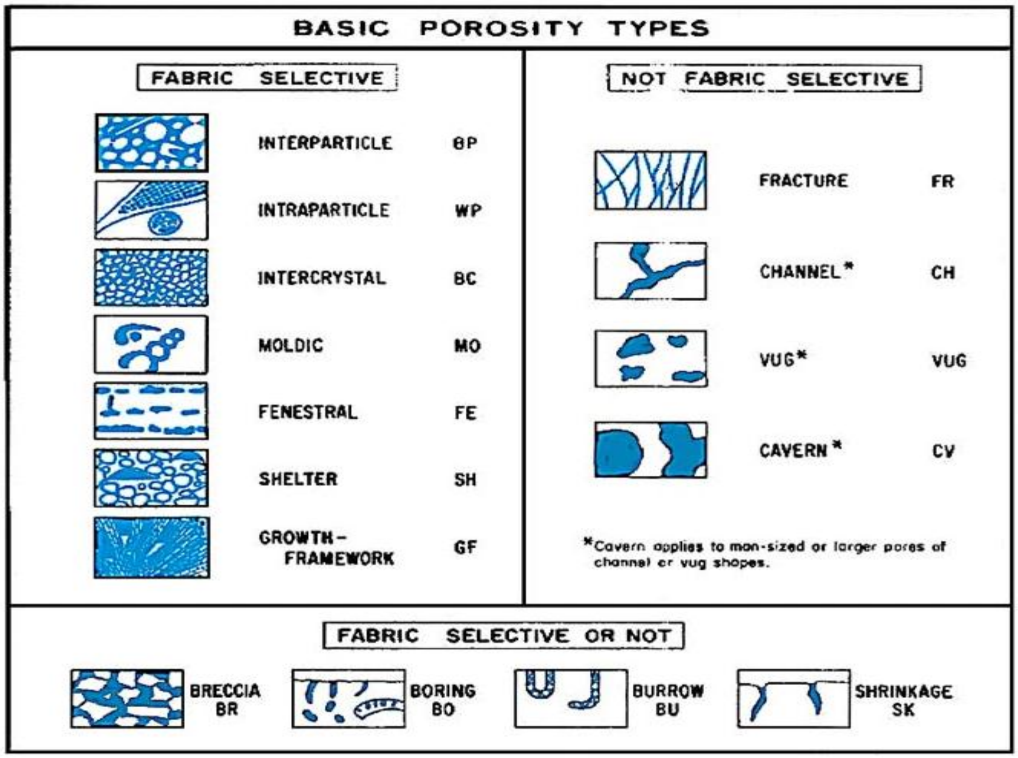

Fig. 3.3—Choquette-Pray Porosity Classification (1970)

Based on Choquette-Pray porosity classification, two categories of porosity present in the Qatar outcrop. **Fig.3.4** shows the fabric selective porosity, most likely to be fenestral (red line direction). It also shows the burrow which falls into the fabric selective or not category.

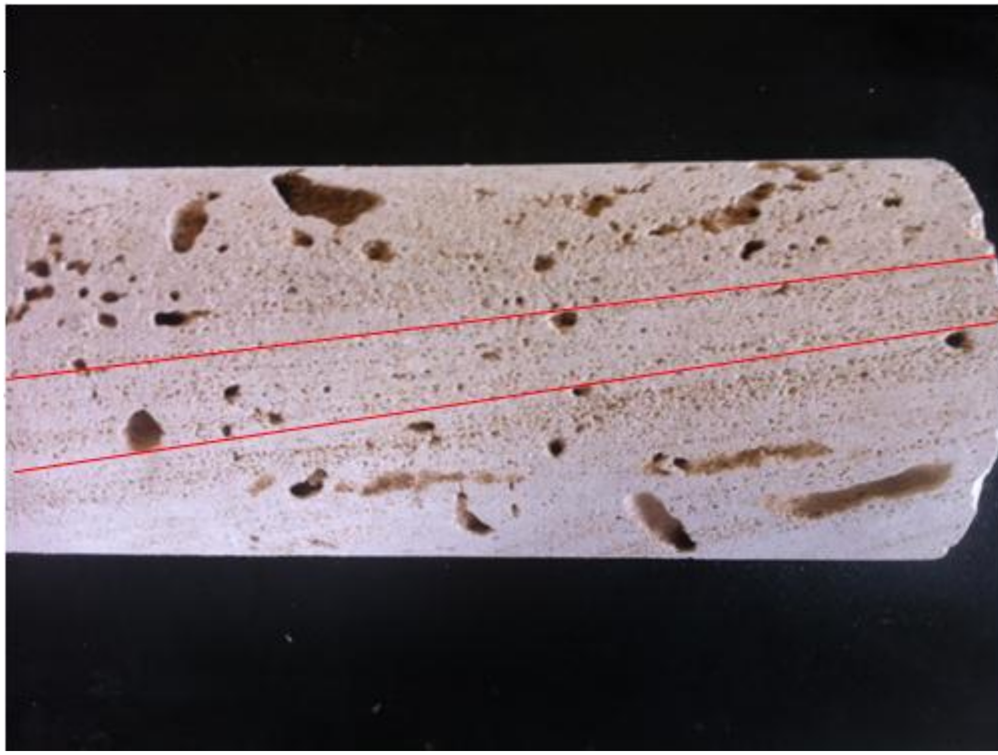

Fig. 3.4—Fenestral and Burrow Porosity Type Presents in Qatar Outcrop

3.2.2 Results and Analysis of 1 inch by 6 inch Experiments

The data of each experiment is shown in **Table 3.2**.The permeability was calculated using the measurement of the pressure drop along the core. The porosity was calculated from the measurement of the dry core weight and saturated weight. The acid injection rates are measured for each experiment.

TABLE 3.2 PROPERTY DATA

No.	Porosity	Permeability (mD)	Acid.Injection Rate(cc/min)	PVbt	Acid Flux(cm/min)
2	0.34	4.39	1.00	0.73	0.59
4	0.35	30.10	3.00	0.31	1.69
10	0.31	2.46	1.00	0.22	0.63
11	0.31	5.53	3.00	0.15	1.89
12	0.34	4.84	3.50	0.05	2.01
13	0.34	1.25	1.25	0.53	0.73
14	0.39	4.20	3.50	0.03	1.77
16	0.35	4.00	4.00	0.18	2.28
18	0.36	18.10	6.00	0.36	3.33
25	0.29	36.00	6.00	0.67	4.07

Variation of porosity and permeability among different experiments can be observed in **Table 3.2**. The log-log plot of porosity and permeability is shown in **Fig.3.5**. The permeability ranges from 1.25mD to 36 mD and the porosity ranges from 0.29 to 0.39. The variation of porosity and permeability is obviously greater than previous homogeneous carbonate studies. Also, there is no clear relationship between porosity and permeability observed from the plot. Vuggy porosity spatial distribution seems to affect the relationship between porosity and permeability since there is a distinct permeability difference of separated vugs (79.6 mD) and connected vugs (2700 mD) in this study on the order of magnitude.

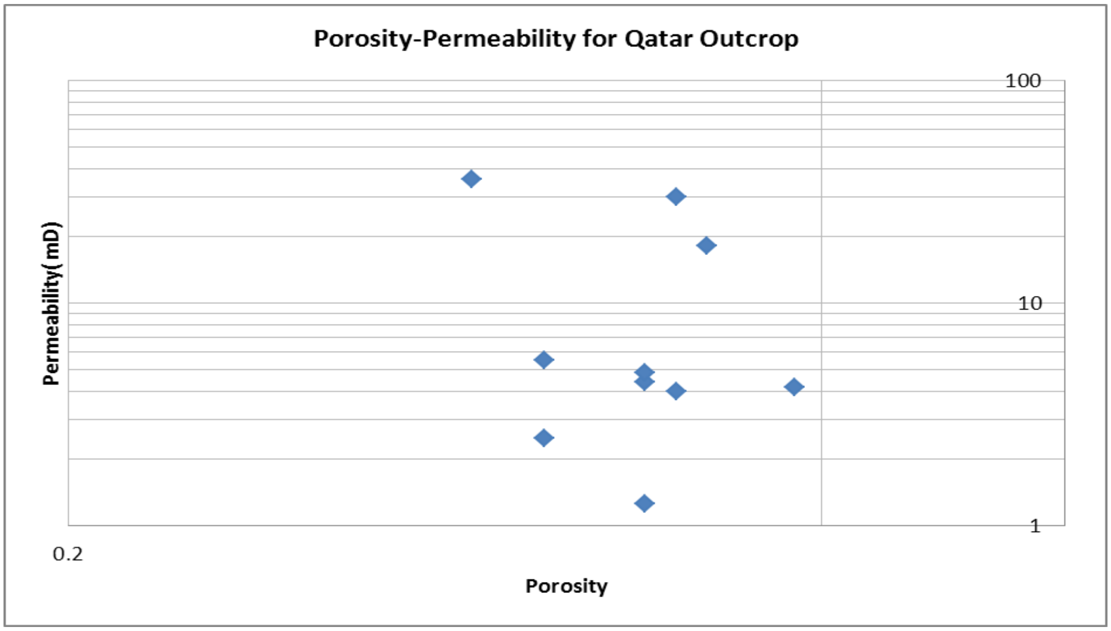

Fig. 3.5—Log-log Plot of Porosity and Permeability

The relationship of acid pore volume to breakthrough and acid flux is shown in **Fig.3.6**. We observed that the optimum acid injection rate exists in heterogeneous rock with separated vugs. The optimum flux is around 2 cm/min when pore volume to breakthrough is around 0.06.

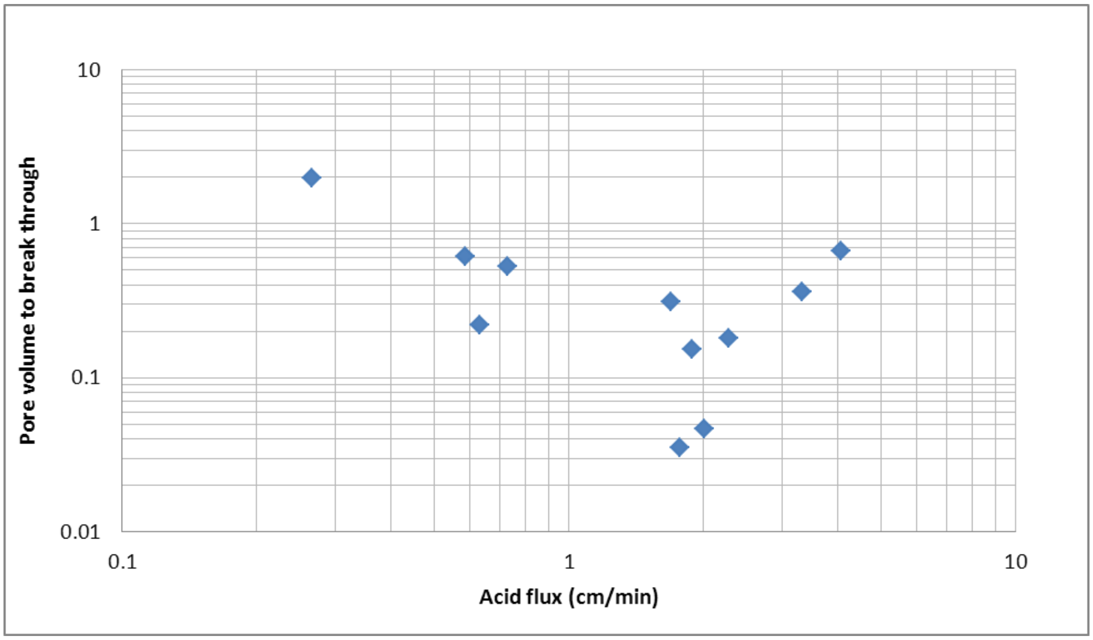

Fig. 3.6 —Optimal Flux for Qatar Outcrop

Omer and Ryan (2008) introduced a term called vuggy porosity fraction in their research. It can be calculated using the vuggy pore divided by the total pore. **Table 3.3** shows the vuggy porosity fraction calculated from the porosity data and CT-Scan numbers in this study. The vuggy porosity fraction ranges from 43% to 74%.

Table 3.3 VUGGY POROSITY FRACTION FOR QATAR OUTCROP

Pore volume to break through	Vi	Vuggy Porosity	Total Porosity	Vuggy Porosity Fraction
1.97	0.27	0.14	0.30	0.47
0.62	0.59	0.15	0.34	0.45
0.31	1.69	0.15	0.35	0.43
0.22	0.63	0.21	0.33	0.64
0.15	1.89	0.17	0.31	0.55
0.05	2.01	0.23	0.31	0.74
0.53	0.73	0.17	0.34	0.50
0.03	1.77	0.26	0.34	0.76
0.18	2.28	0.17	0.39	0.44
0.36	3.33	0.18	0.34	0.53
0.67	4.07	0.14	0.29	0.48

Omer and Ryan (2008) draw the conclusion that: ‘The PV_{BT} for vuggy limestone correlates inversely with the fraction of total porosity comprised by vugs – the higher the vuggy fraction of porosity, the lower the pore volumes to breakthrough.’ As mentioned earlier, for the same set of experiments, different acid flux will lead to different acid response to rock and the measurements of pore volume to breakthrough will be different accordingly. Since the variation of acid flux in this study is much greater than Omer and Ryan’s study, the influence of acid flux on the pore volume to breakthrough number cannot be neglected. In order to minimize the influence, the results of pore volume to breakthrough are selected among which differences of the corresponding acid flux are not larger than 1 cm/min. **Fig.3.7** shows these data. Two groups of data were selected with the differences of acid flux around or less than 0.1.

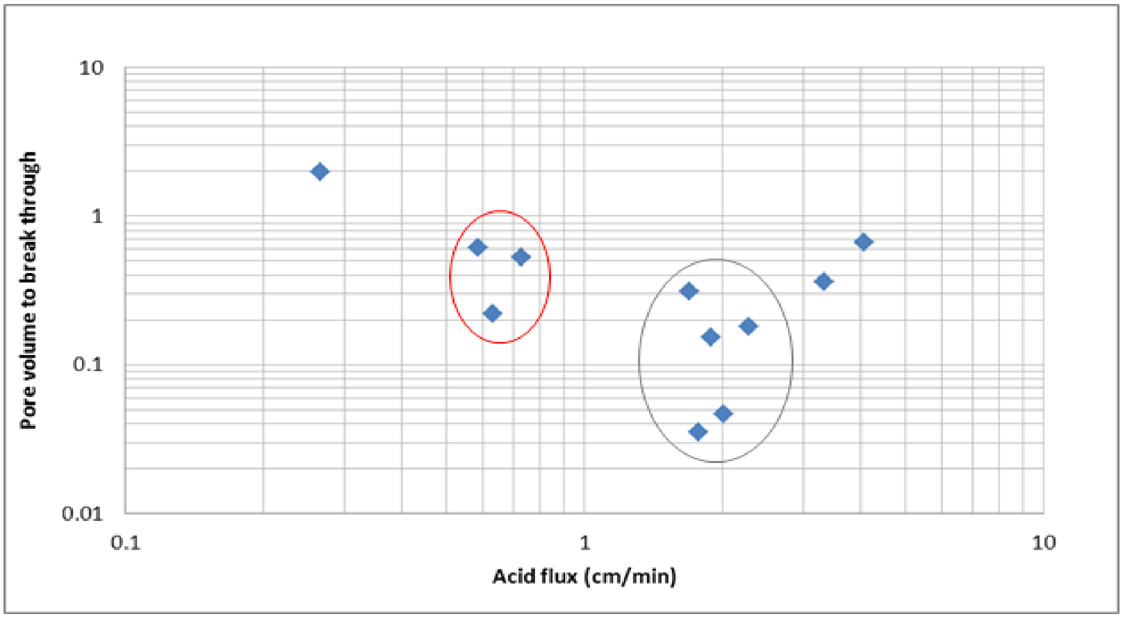

Fig. 3.7—Data Selection to Minimize the Acid Flux Influence

Fig 3.8 show the presences of vugs contribute to the early breakthrough of acid when the difference of acid flux among each data is around or less than 0.1cm/min. Although the size of the cores using in the experiment is different from Omer and Ryan's study, we draw the similar conclusion by only adding consideration of acid flux influence.

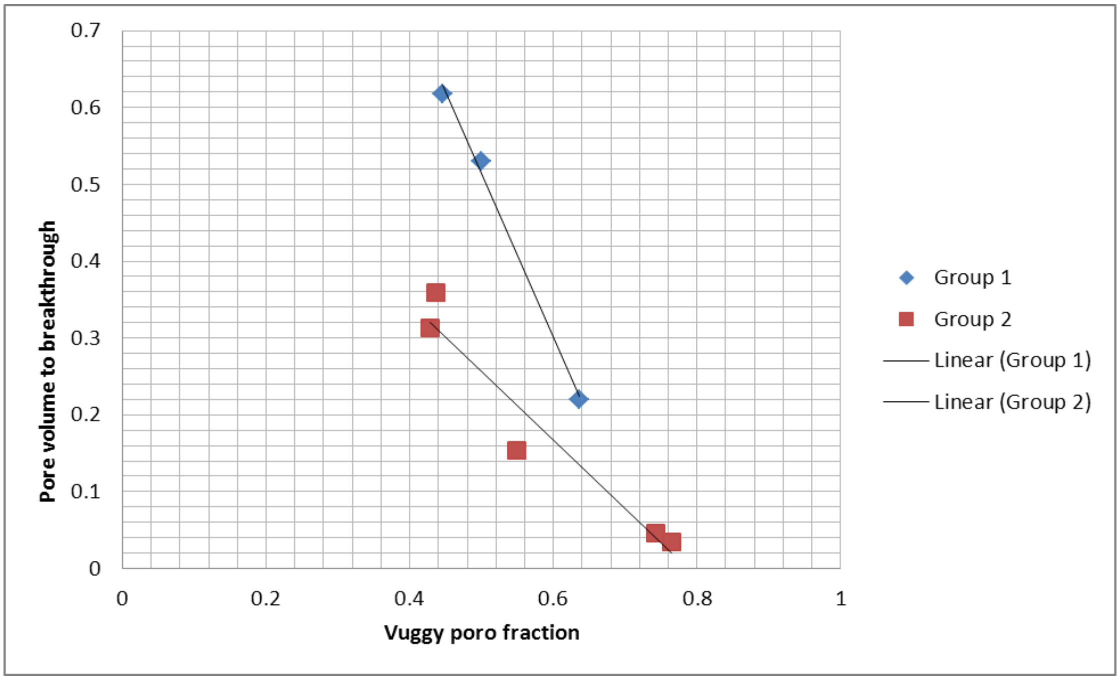

Fig. 3.8—Experimentally Observed Relation between Total Vuggy Pore Space and *PVbt*

Fig.3.9 shows the CT-Scan images with the core before acidizing(left) and after acidizing (left). The core has separated vugs and channels. From the comparison of the CT-Scan before and after the acidizing experiment, the acid flow path tends to connect most of the separated vugs and channels. The vugs spatial distribution not only contributes to the early breakthrough of acid, but also affects the acid flow regime and wormhole pattern.

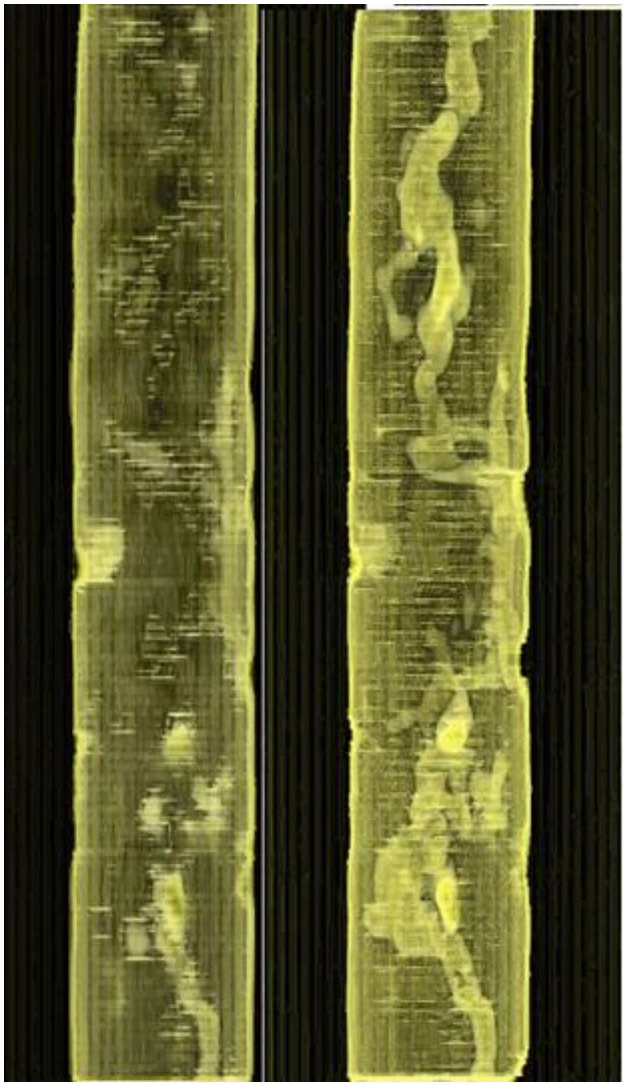

Fig. 3.9—CT- Scan Image of before and after Acidizing Experiment

The comparison of vuggy carbonate with Wang's (1993) homogeneous carbonate is shown in **Fig 3.10**. Wang's experiments were conducted under different temperature and different acid concentrations. The comparison is made in the cores of same size and the red dots show the data from this study. All the pore volume to breakthrough from this study is lower than previous measurements. The optimal injection rate curve shifts down. Data from green color was pursued from the same experiment condition using homogenous carbonate. Heterogeneity will lead to a smaller pore volume to breakthrough number.

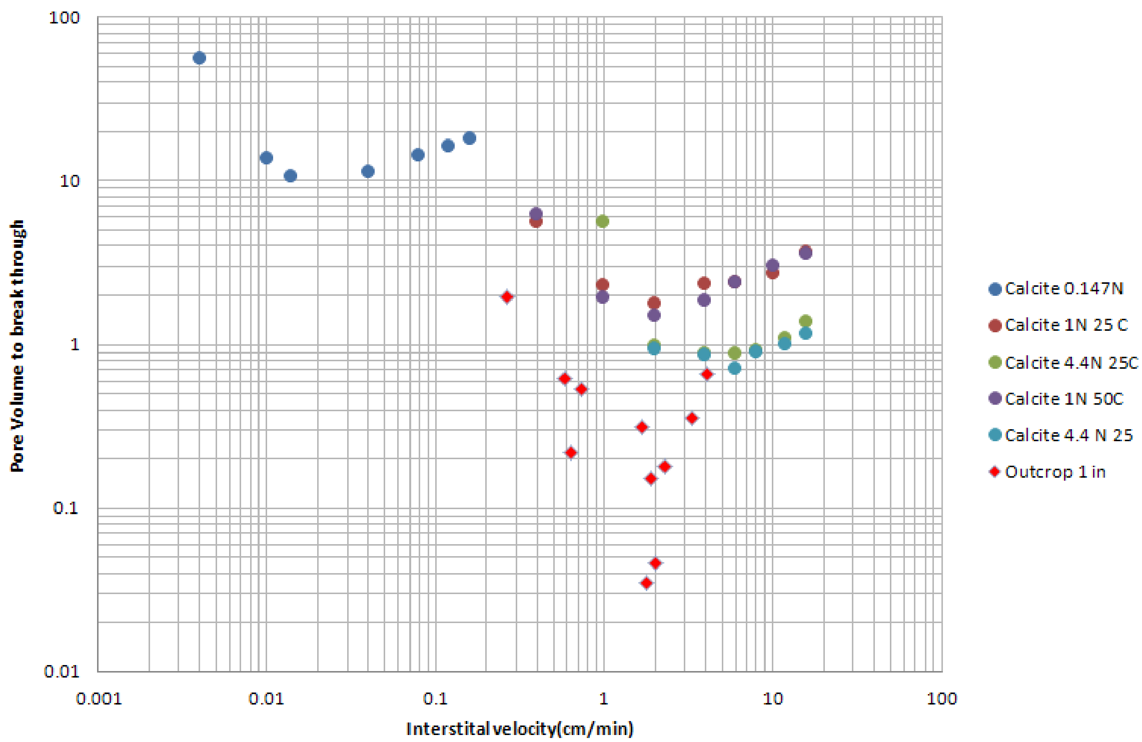

Fig. 3.10—Comparison of Pore Volume to Breakthrough

3.2.3 Results and Analysis of 4 inch Diameter by 18 inch Core

The purpose of conducting experiments using 4 inch diameter by 18 inch core is to study the effect of connected vugs and channels on acid stimulation. One experiment was conducted under the same experiment condition as 1 inch diameter by 6 inch cores and the other one was conducted after damaging the core with drill-in fluid before acidizing.

1) Large diameter core without drill-in fluid damage

Fig.3.11 shows the appearance of 4 inch diameter and 18 inch length core before acidizing **Fig.3.12** shows the CT-Scan of the core before(left) and after (right) acidizing .

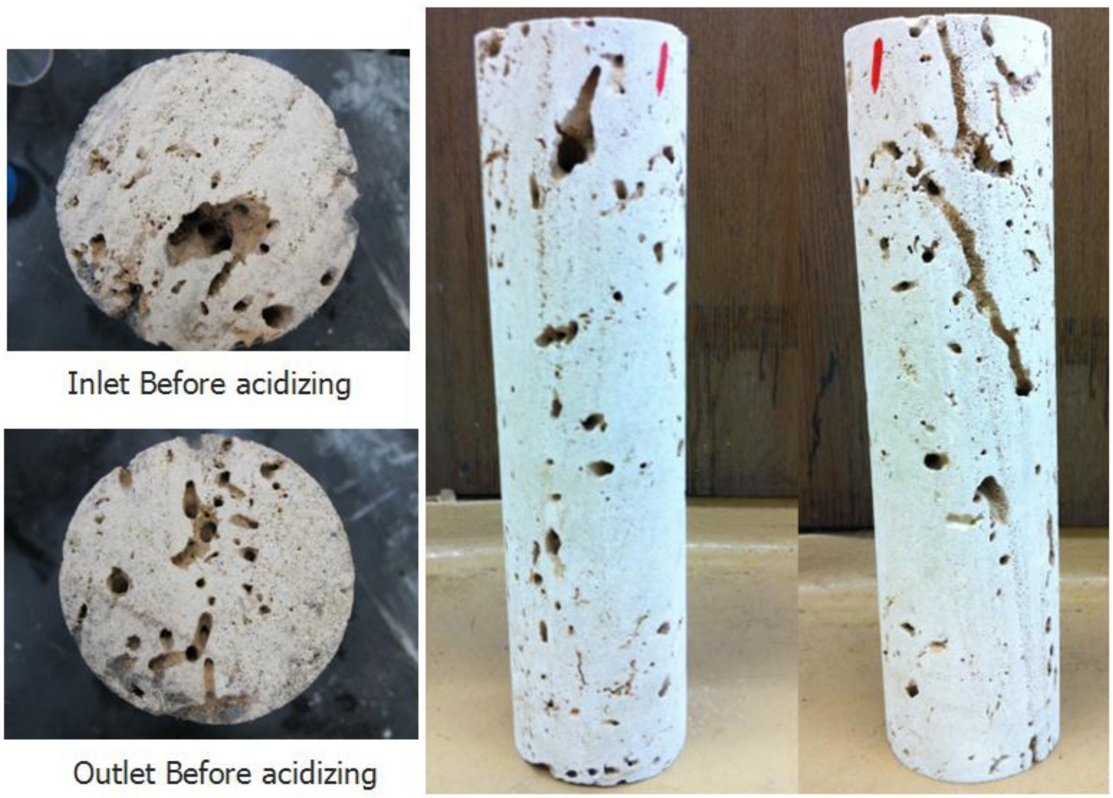

Fig. 3.11—Vuggy Nature of Carbonate Experiment Core

It can be observed from the CT-Scan image that connected vugs and channels exist in the core. The permeability was measured to be 2680 mD. Even though the core holds the same matrix density, the measured permeability is more than 100 times larger than 1 inch by 6 inch length cores. The vugs spatial distribution (separated or connected) has huge effect on the permeability of the vuggy carbonate.

Fig. 3.12—CT-Scan Image before(Left) and after(Right) the Acidizing Experiment

Fig.3.13 shows the CT-number profile from the inlet (left side) to the outlet (right side) of the core. The reading from the y-axis on the plot represents the average CT-number from individual CT-slide. The reading from x-axis represents the slice's number. Higher CT number represents objects with higher density, and vice versa. After acidizing, the CT-number decreases in the range from 5 to 50 along the whole core, This indicates the density of the core slightly decreases after acidizing experiment.

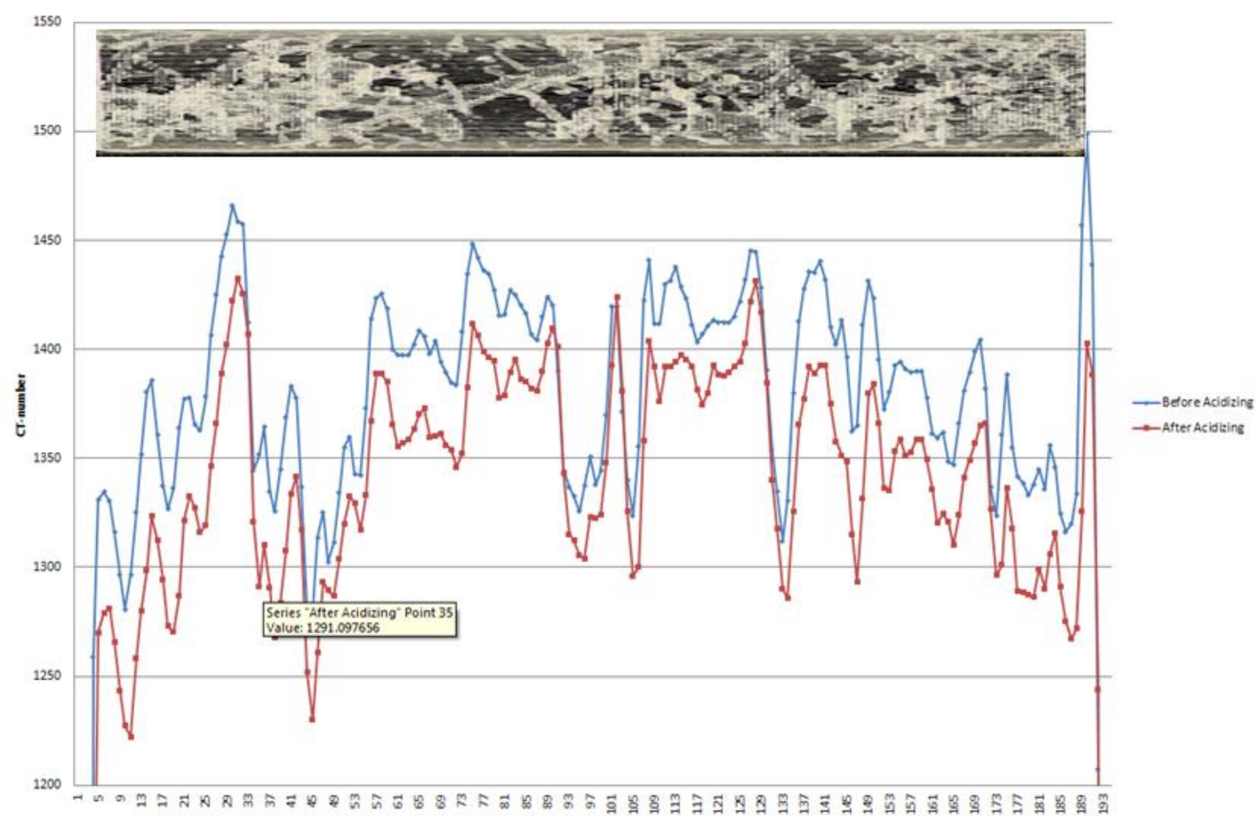

Fig. 3.13—CT-number Profile along the Core before Acidizing (Blue) and after Acidizing(Red).

In order to understand how acid react with rock in the connected vugs and channels, the CT-Scan results are analyzed. **Fig.3.14** shows the comparison of CT-Scan from the same position on the core before (left picture) and after (right picture) acidizing. The area of black color represents the vuggy pore space in the core and area of white color represents the matrix. It is observed that acid tend to create new pore space by dissolving the carbonate matrix near the existing vuggy pore space.

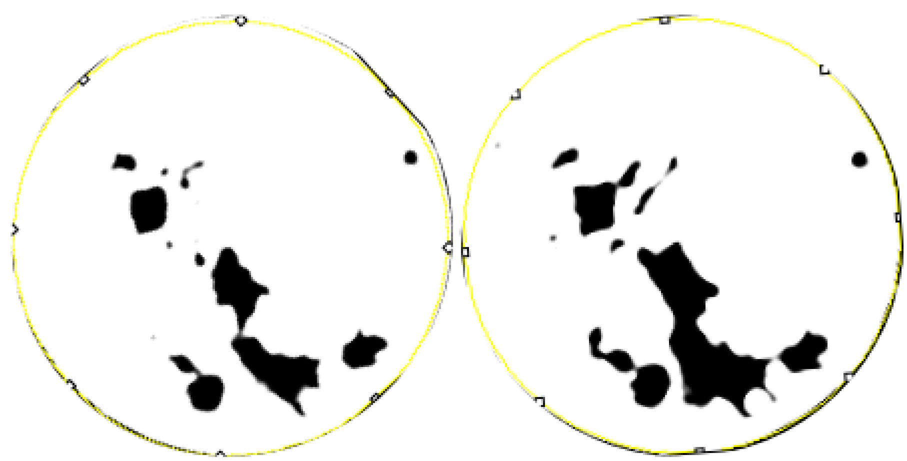

Fig. 3.14—Vuggy Pore Space Comparison before (Left) and after (Right) the Experiment

2) Large diameter core with drill-in fluid damage

Fig.3.15 shows the drilling mud contamination from external and internal of the core. The right picture is the CT-Scan with the contrast color of red (indicate mud) and yellow (indicate vugs and channels). It is observed that the contamination of drill-in fluid is quite severe even with only 50 psi pressure applied on the inlet of the core. Nearly all the major channels are full of drilling mud. The original permeability is close to 3000 mD, and the permeability after contamination is measured to be 79.6 mD. It requires 6.7 min acid injection time with acid injection rate of 15 cc per min to bypass the drill-in fluid damage zone.

Fig. 3.15—Core with Drill-in Fluid Contamination

The comparison of CT-numbers of ordinary core, core with drill-in fluid damage and core after acid treatment is shown in **Fig.3.16.** The reading from the y-axis on the plot represents the average CT-number from individual CT-slide. The reading from x-axis represents the slide's number. After the vuggy pore space is filled with drill-in fluid, the CT-number will go higher which means that average density will go higher accordingly. For the core with drill-in fluid, it is observed that before acidizing, the CT-number of the inlet is larger than that of the outlet. This is because the drill-in fluid would accumulate more on the inlet than the outlet. After acidizing the density of the core decreases , which is close to the original density before drill-in fluid damage.

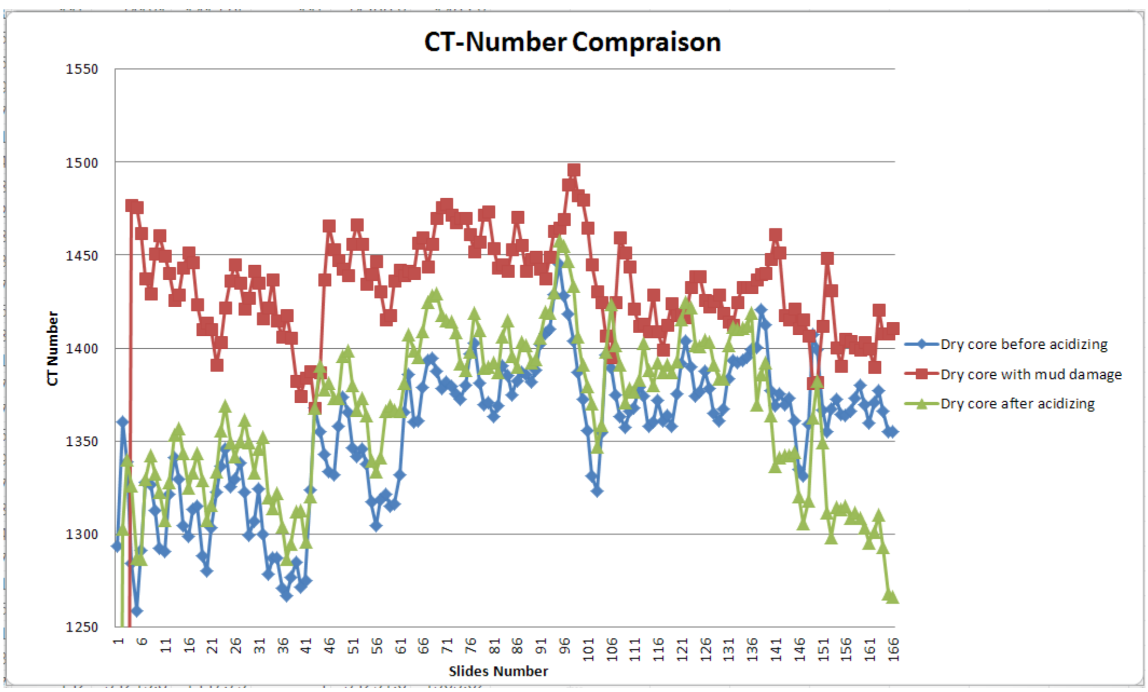

Fig.3.16—CT-number Comparison

The comparison of CT-Scan before and after acid experiment is shown in **Fig.3.17**. We can tell that the acid by pass the damage zone by dissolving the matrix of the carbonate nearby the existing vuggy pore space.

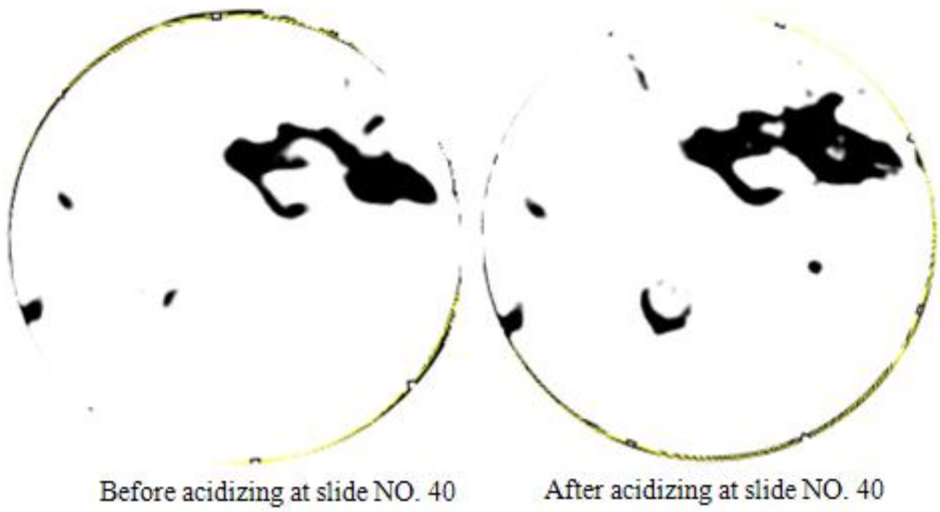

Fig.3.17—CT Image Comparison

CHAPTER IV

CONCLUSIONS

This study presents an experimental study on the response of acid to rocks with two types of rocks: Homogeneous carbonate and heterogeneous carbonate. Separated studies were done with heterogeneous carbonate with separated vugs and channels and heterogeneous carbonate with connected vugs and channels. Important development and conclusions can be summarized as:

1. The optimal injection rate exists for homogenous core. The optimal acid flux was found to be 0.41 and pore volume to break through is 0.23 accordingly.
2. Vuggy porosity spatial distribution affects the permeability. There is a distinct permeability difference of separated vugs and connected vugs in this study.
3. The acid flow path tends to connect the separated vugs and channels. The existing vugs not only contribute to the early breakthrough of acid, but also affect the acid flow regime and wormhole pattern.
4. The optimum injection rate for heterogeneous carbonate with separated vugs and channels exists. The optimum flux for separate vugs and channels with vuggy porosity fraction range from 43% to 76% is around 2 when pore volume to breakthrough is around 0.06 with the vuggy porosity fraction ranges from 43% to 74% in this study.
5. Within the similar acid flux, the corresponding PV_{BT} for vuggy limestone correlates inversely with the fraction of total porosity comprised by vugs.

6. Vuggy carbonates with connected vugs and channels, whether or not formation damage exists, the acid tends to create new pore space nearby the existing vugs and channels.

7. Drill-in fluid can reduce the permeability of the carbonates with channels and vugs from nearly 3000mD to 79.6 mD with 50 psi overbalance pressure applied. Acid treatment is able to restore the productivity via bypassing the damage zone successfully.

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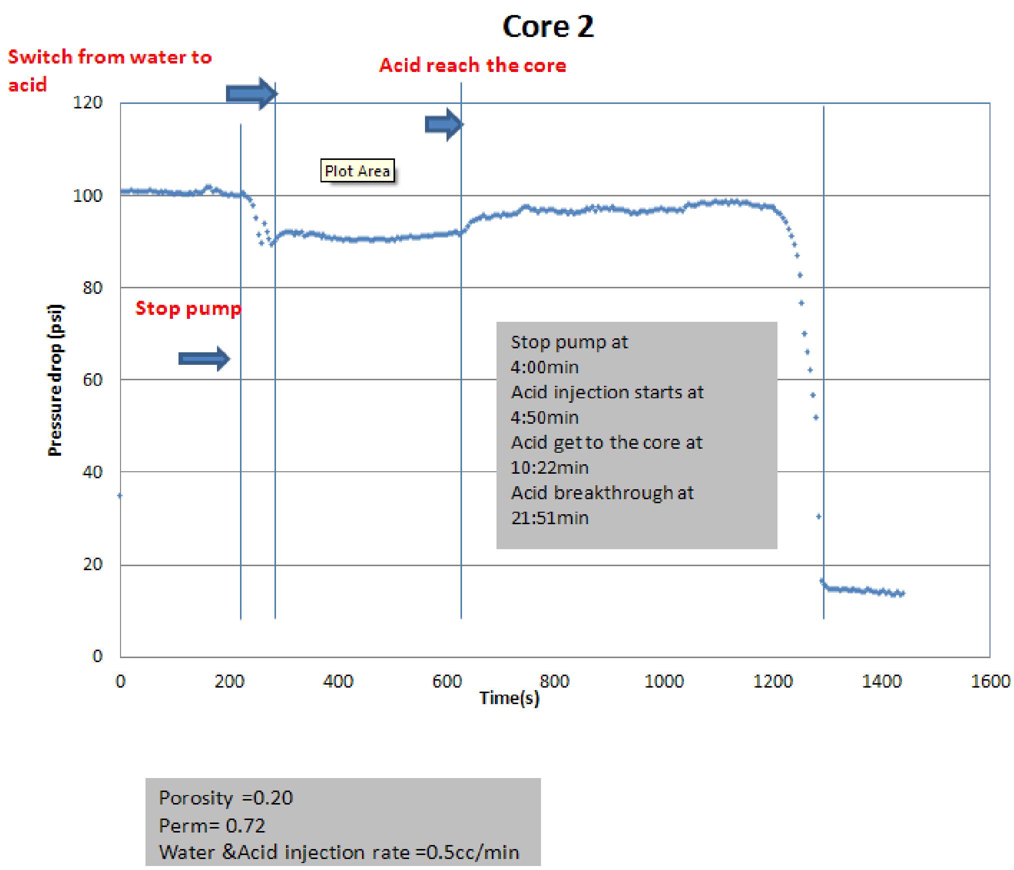
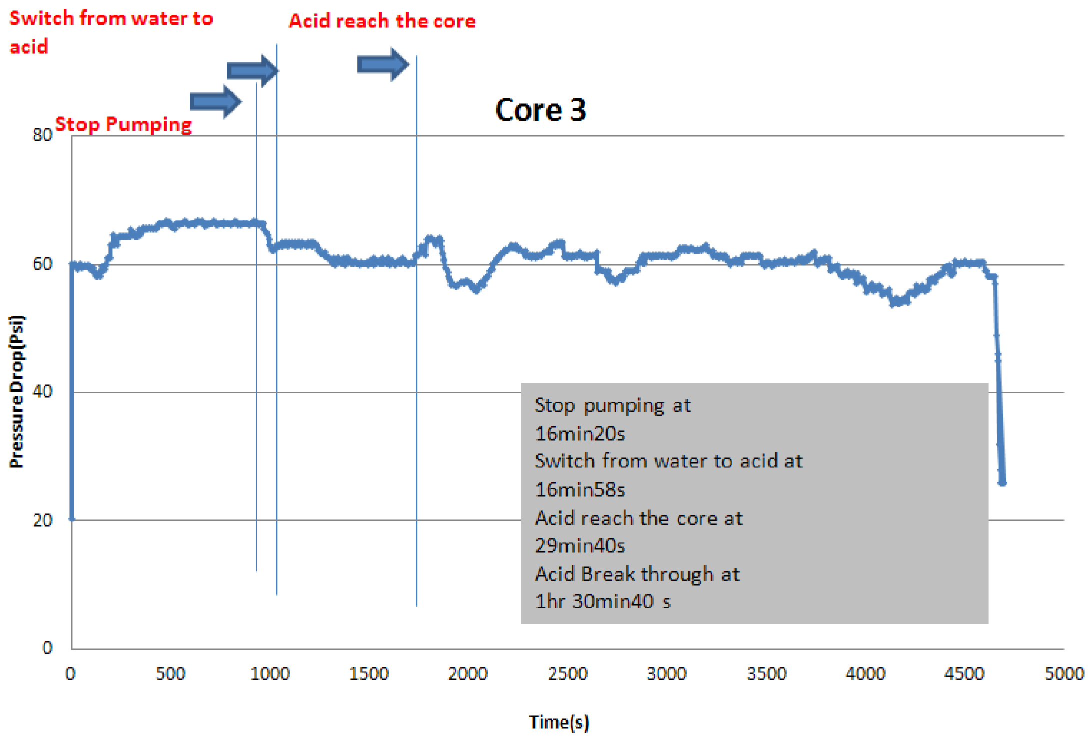
APPENDIX A

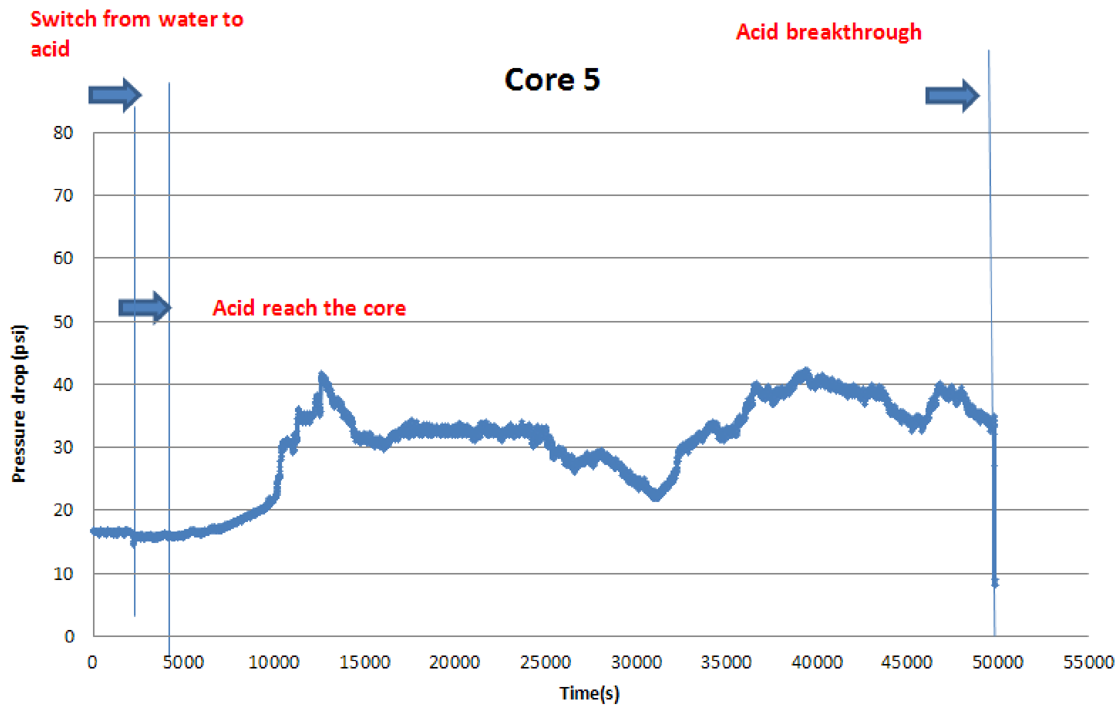
PRESSURE AND EXPERIMENT DATA FOR HOMOGENEOUS TRIAL PLUGS



Note: All the permeability values were measured in mD

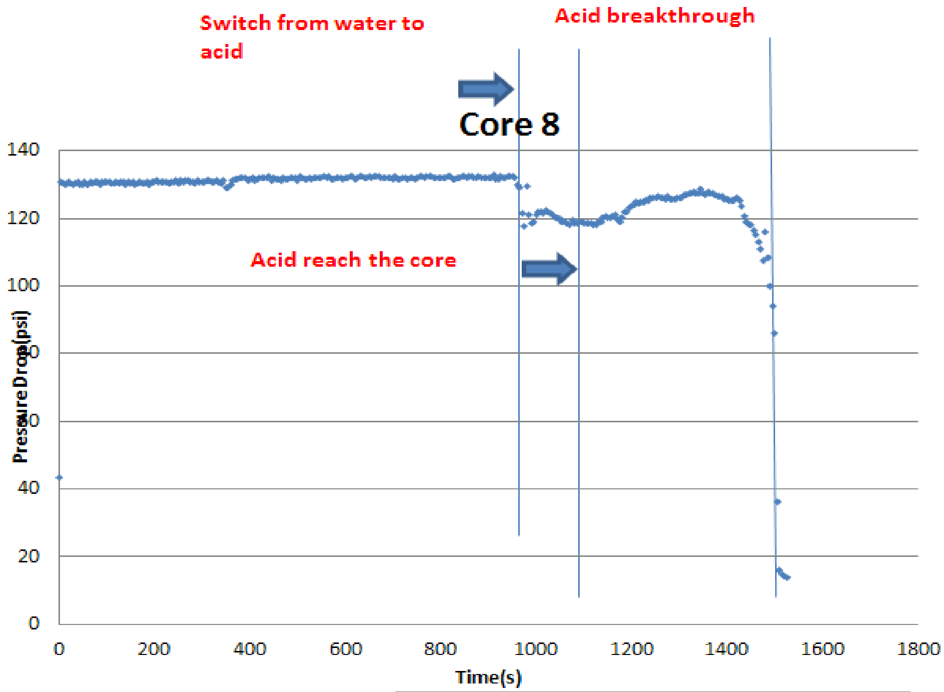


Porosity =0.14
Perm= 0.63
Flux= 0.17cm/min
PVbt= 1.29



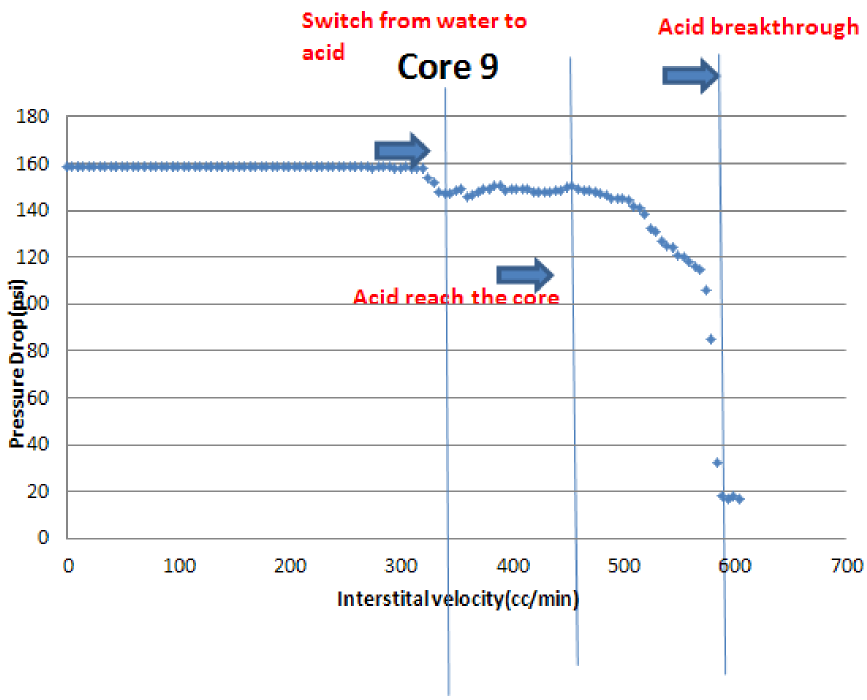
Porosity =0.18
Perm= 0.97
Flow rate= 0.1cc/min
Flux= 0.05cm/min
PVbt= 6.04

Stop pumping at
36min40s
Switch from water to acid at
37min10s
Acid reach the core at
1hr5min16s
Acid Break through at
1hr 30min40 s



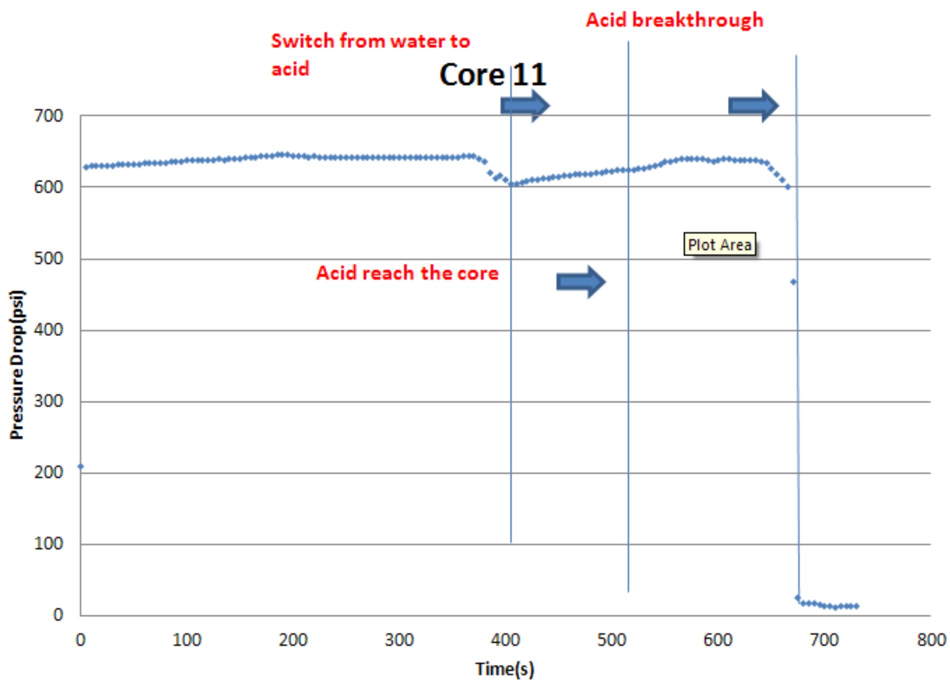
Porosity =0.23
Perm= 1.09
Flow rate= 1cc/min
Flux= 0.41cm/min
PVbt= 0.23

Stop pumping at 15min48s
Switch from water to acid at 16min27s
Acid reach the core at 18min59s
Acid Break through at 25min10s



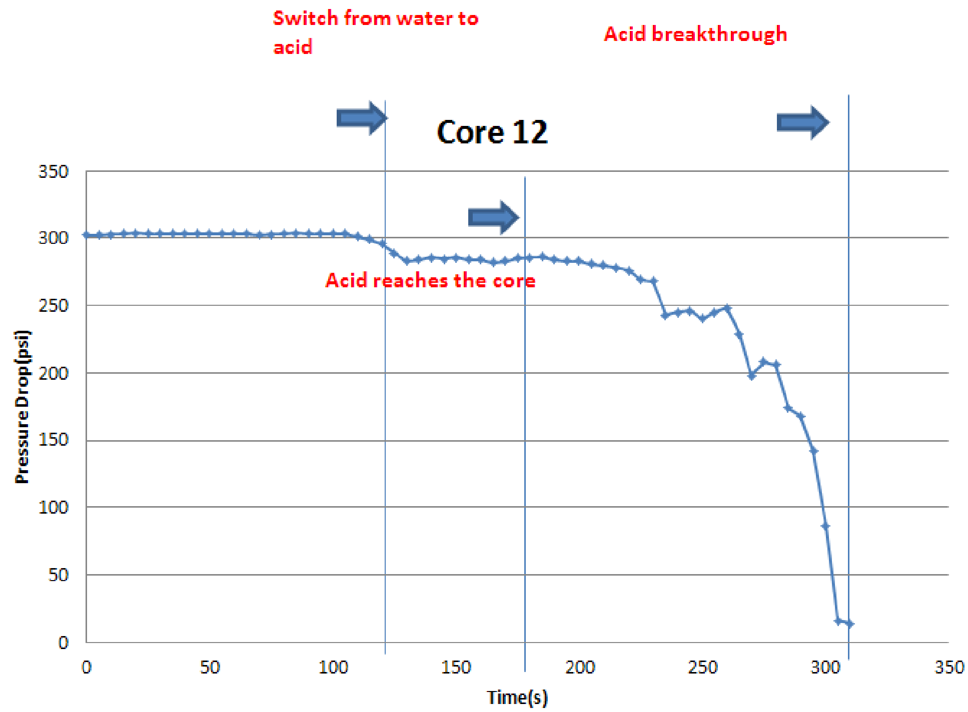
Porosity =0.21
Perm= 0.98
Flow rate= 1.15cc/min
Flux= 0.5 cm/min
PVbt= 0.27

Stop pumping at
5min18s
Switch from water to acid at
5min35s
Acid reach the core at
8min01s
Acid Break through at
12min13s



Stop pumping at
6min00s
Switch from water to acid at
6min37s
Acid reach the core at
8min50s
Acid Break through at
13min25s

Porosity =0.20
Perm= 0.33
Flow rate= 1.5cc/min
Flux= 0.67cm/min
PVbt= 0.29



Stop pumping at 1min45s
Switch from water to acid at 2min05s
Acid reach the core at 3min18s
Acid Break through at 5min10s

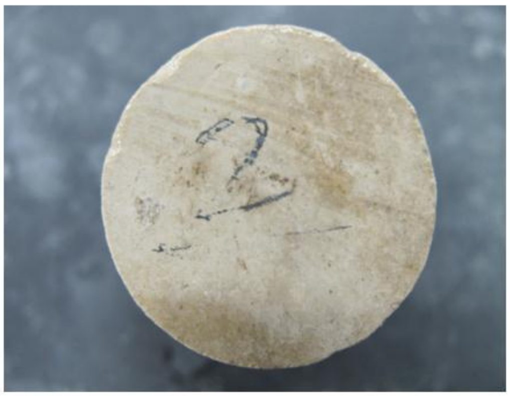
Porosity =0.20
Perm= 1.3
Flow rate= 2.5cc/min
Flux= 1.20 cm/min
PVbt= 0.36

APPENDIX B

PHOTOGRAPH OF HOMOGENEOUS CARBONATE BEFORE AND AFTER EXPERIMENT

Inlet

Before **After**



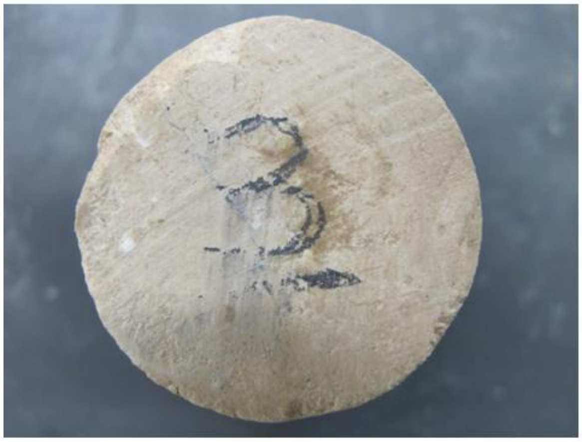
Outlet

Before **After**

Core 2

Inlet

Before **After**



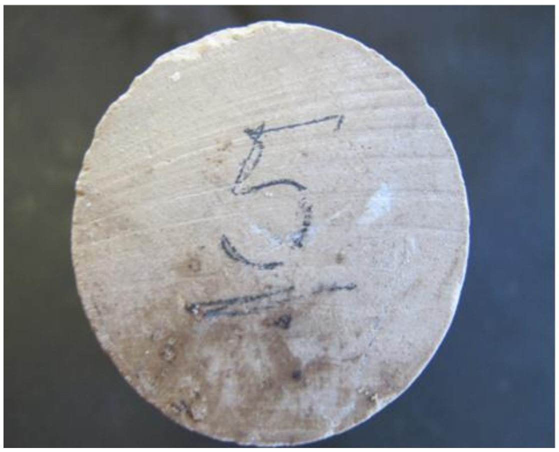
Outlet

Before **After**

Core 3

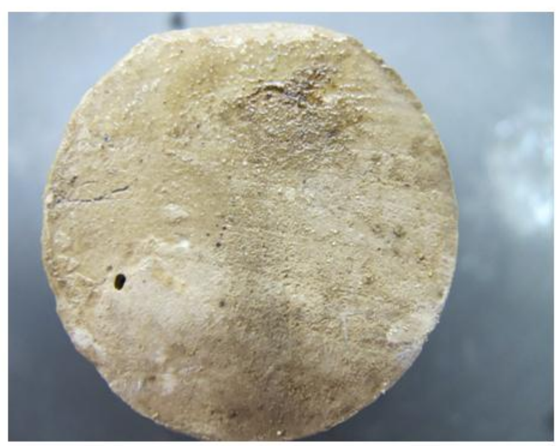
Inlet

Before **After**

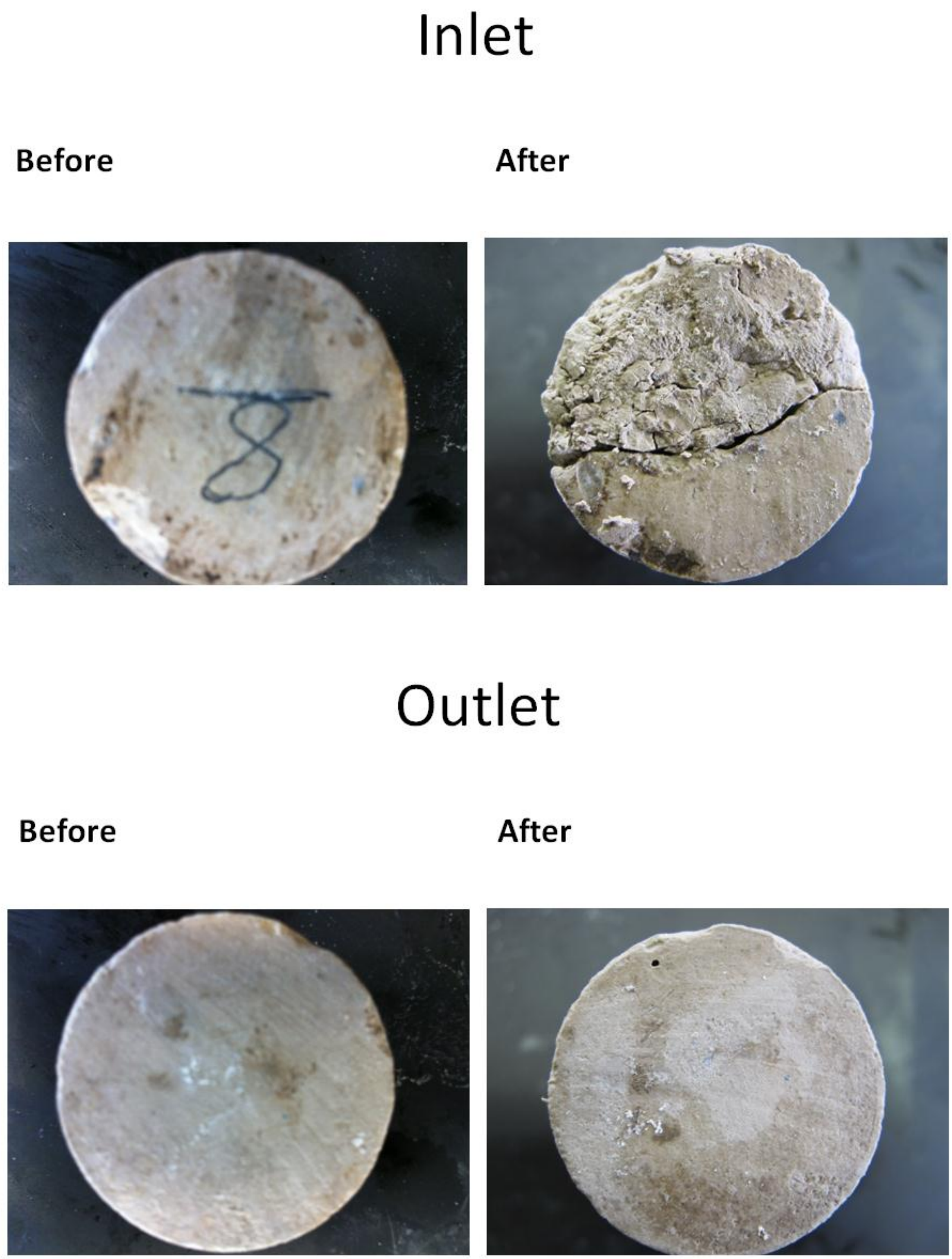


Outlet

Before **After**



Core 5



Core 8

Inlet

Before **After**


Outlet

Before **After**


Core 9

Inlet

Before **After**

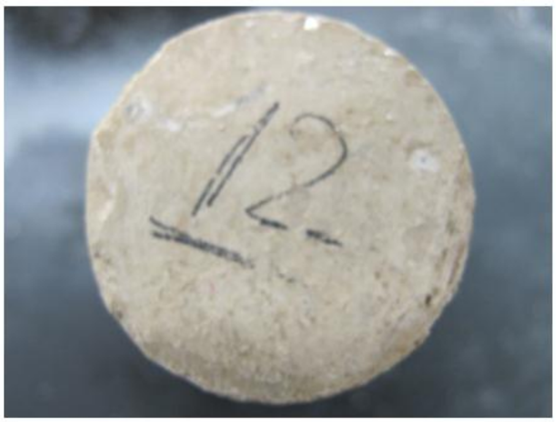
Outlet

Before **After**

Core 11

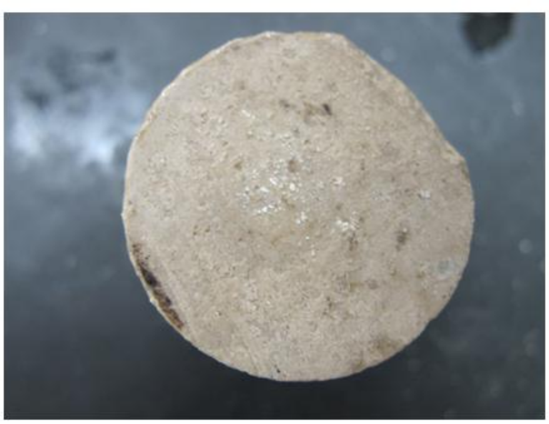
Inlet

Before **After**



Outlet

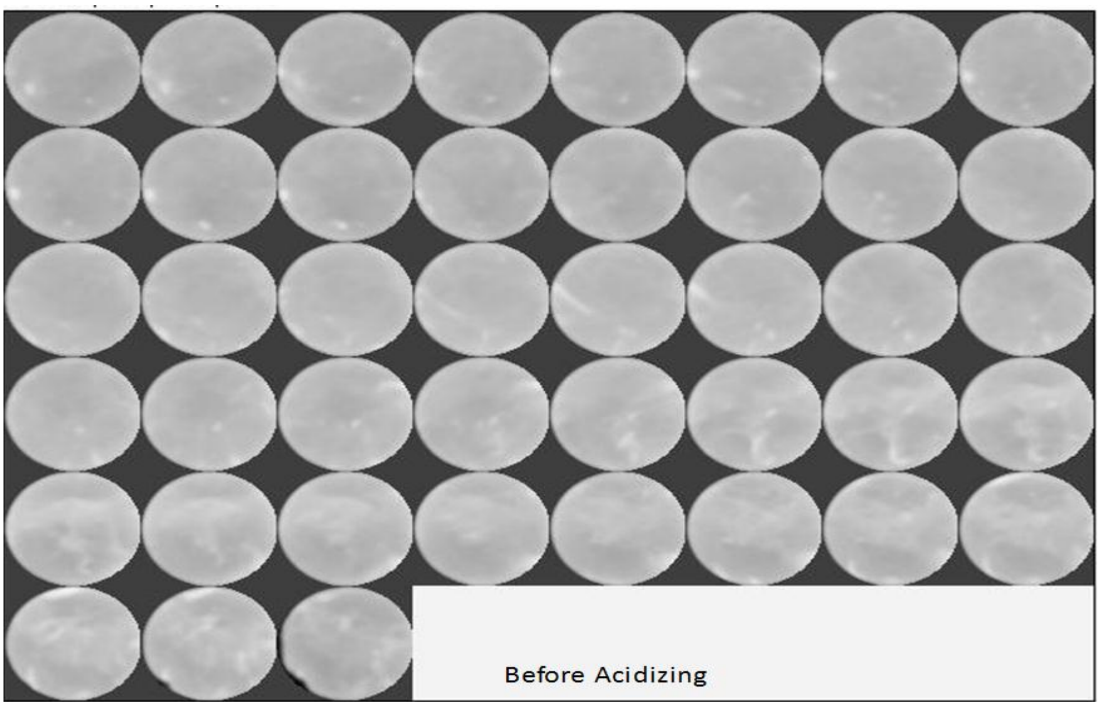
Before **After**

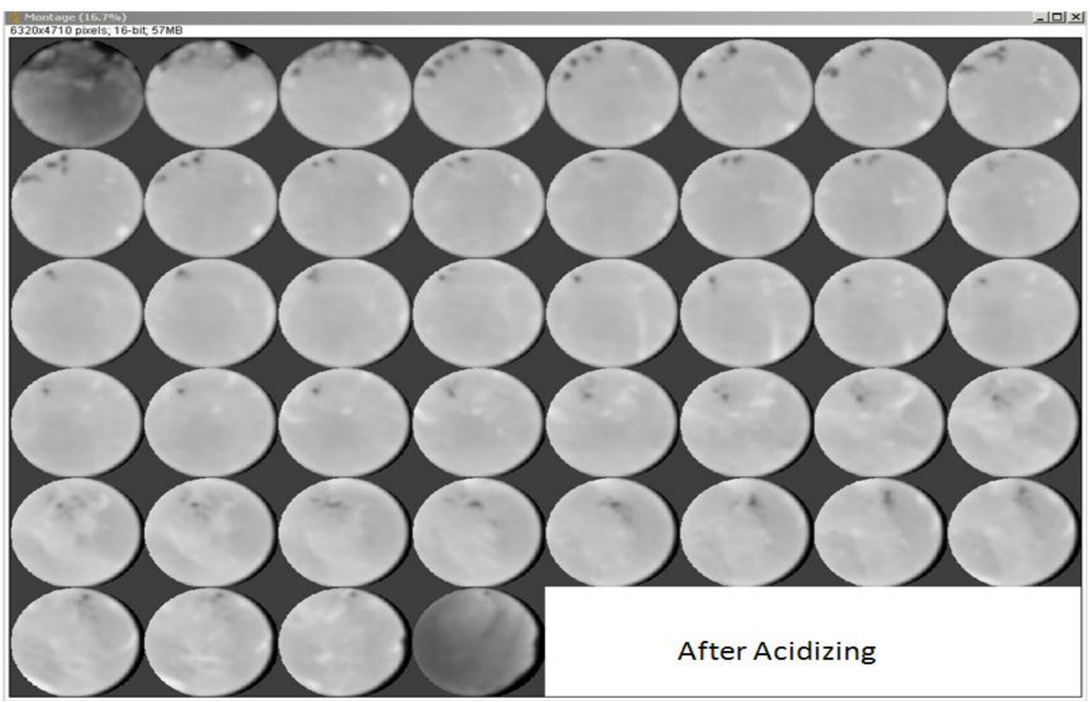


Core 12

APPENDIX C

PICTURES FOR HOMOGENEOUS TRIAL PLUGS BEFORE AND AFTER EXPERIMENT


Before Acidizing


Montage (16.7%)
6320x4710 pixels; 16-bit; 57MB
After Acidizing

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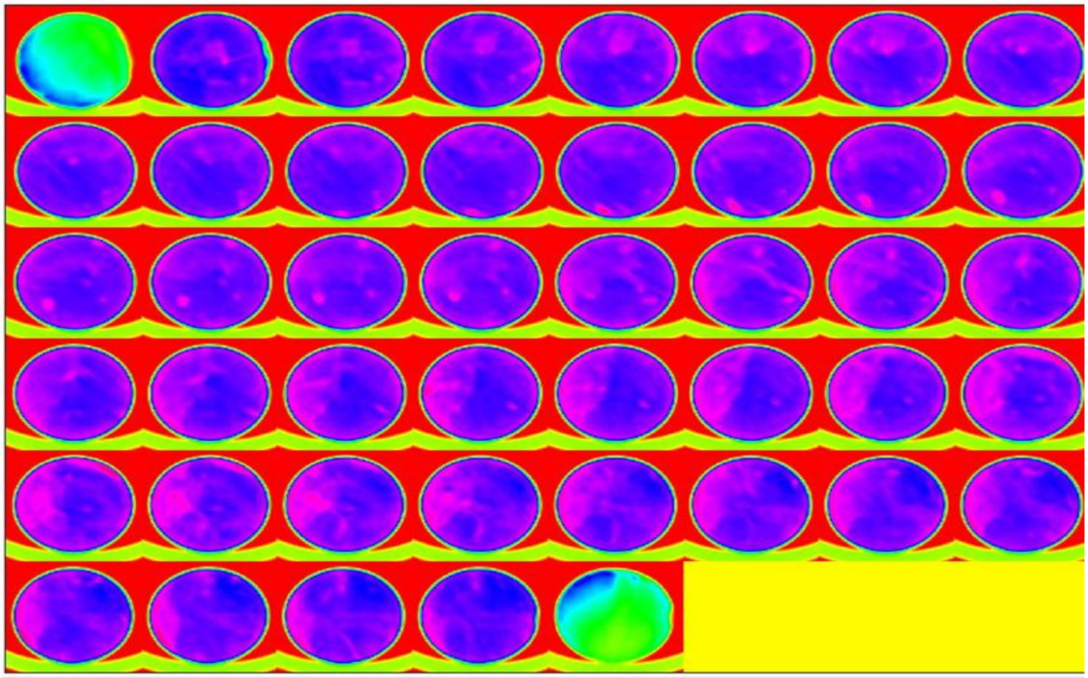

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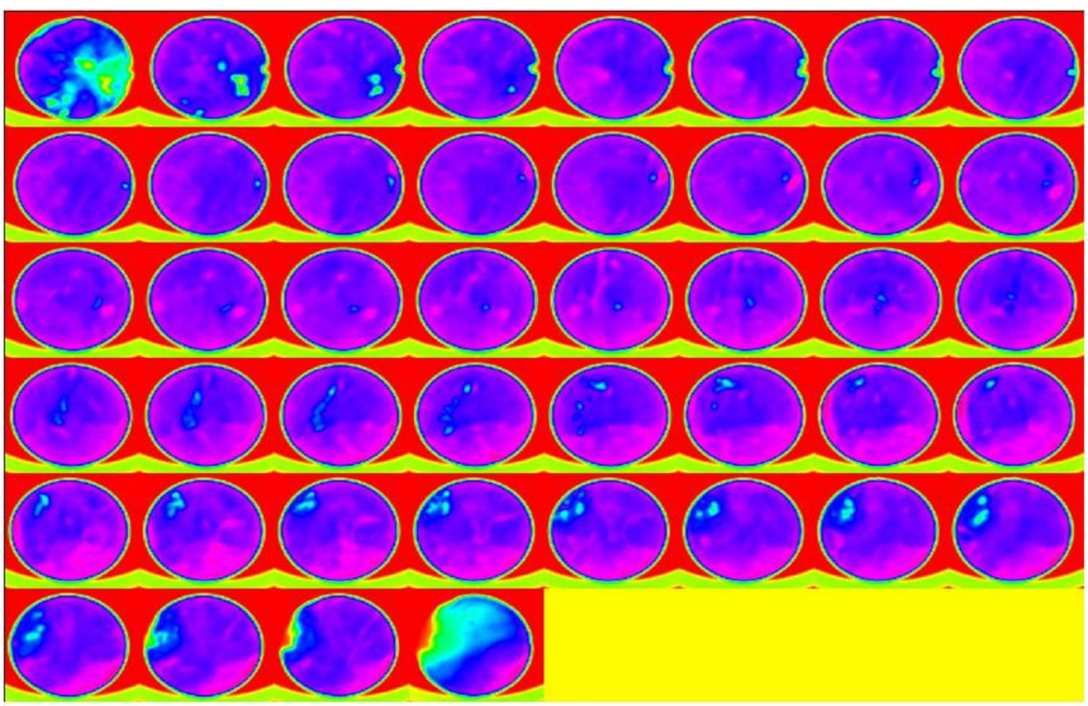

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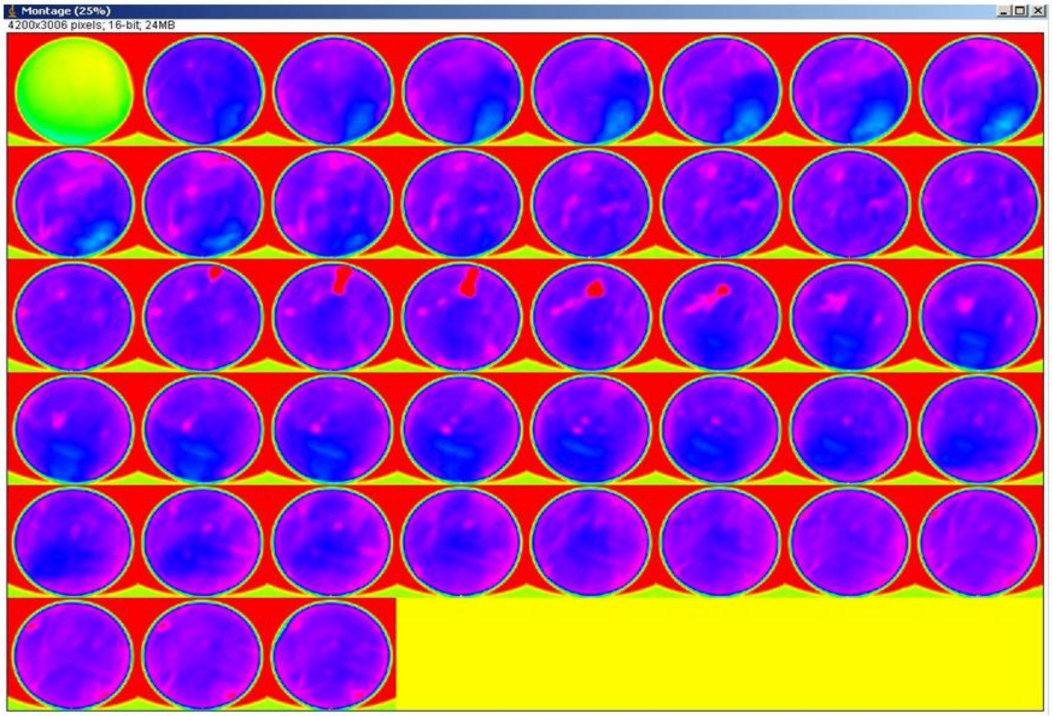

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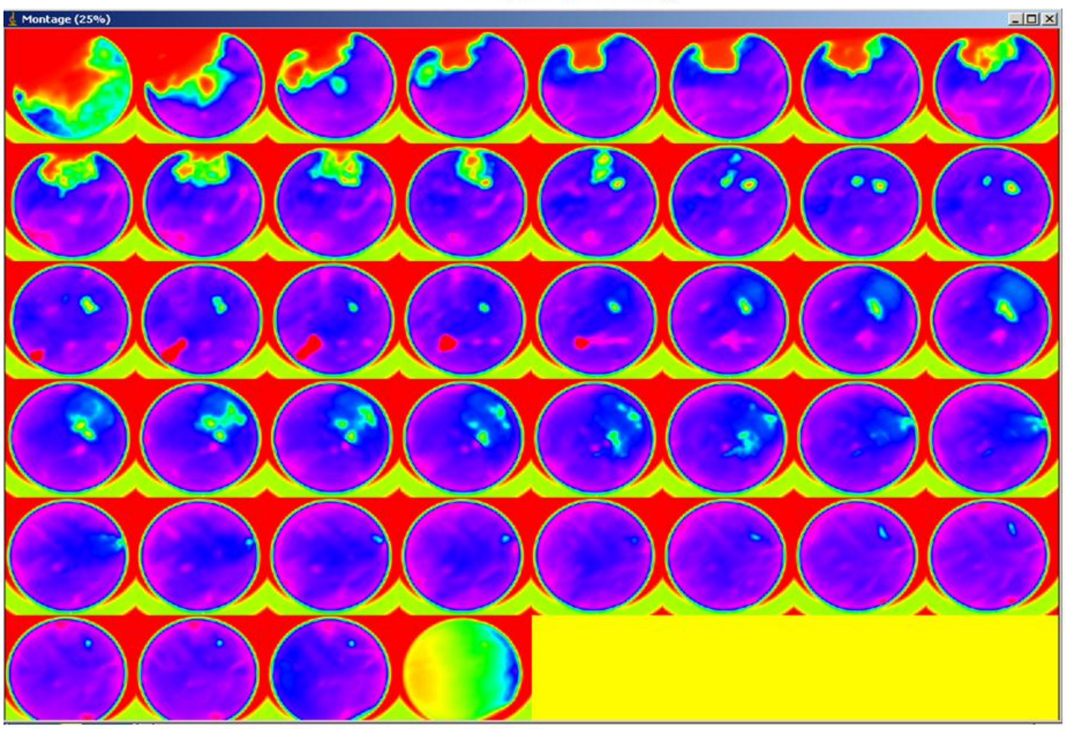

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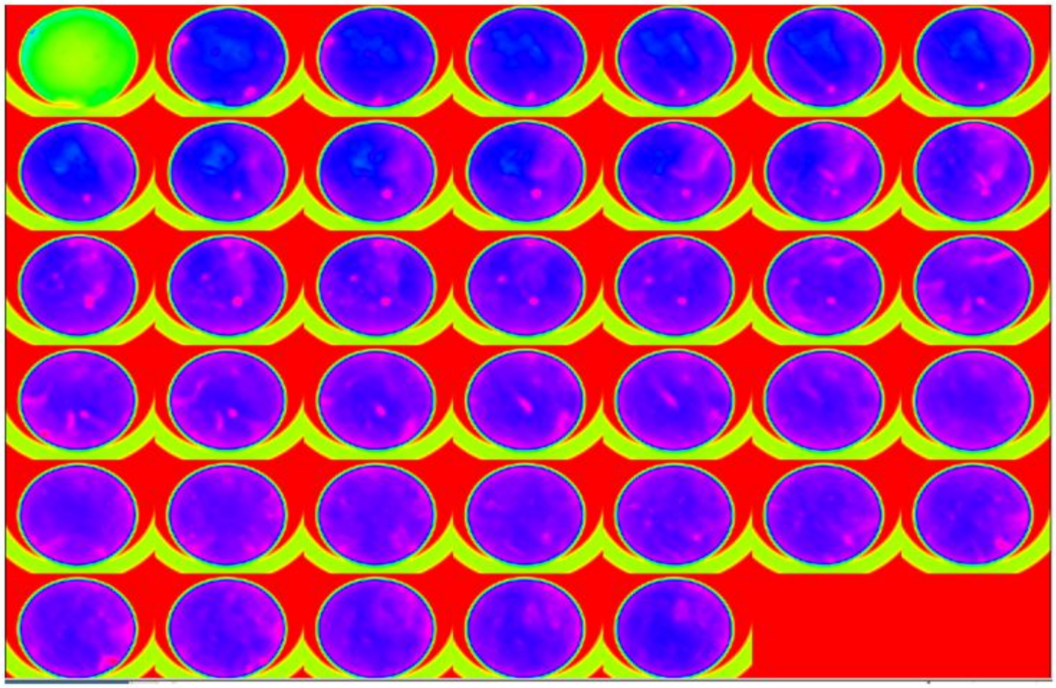
Core 5



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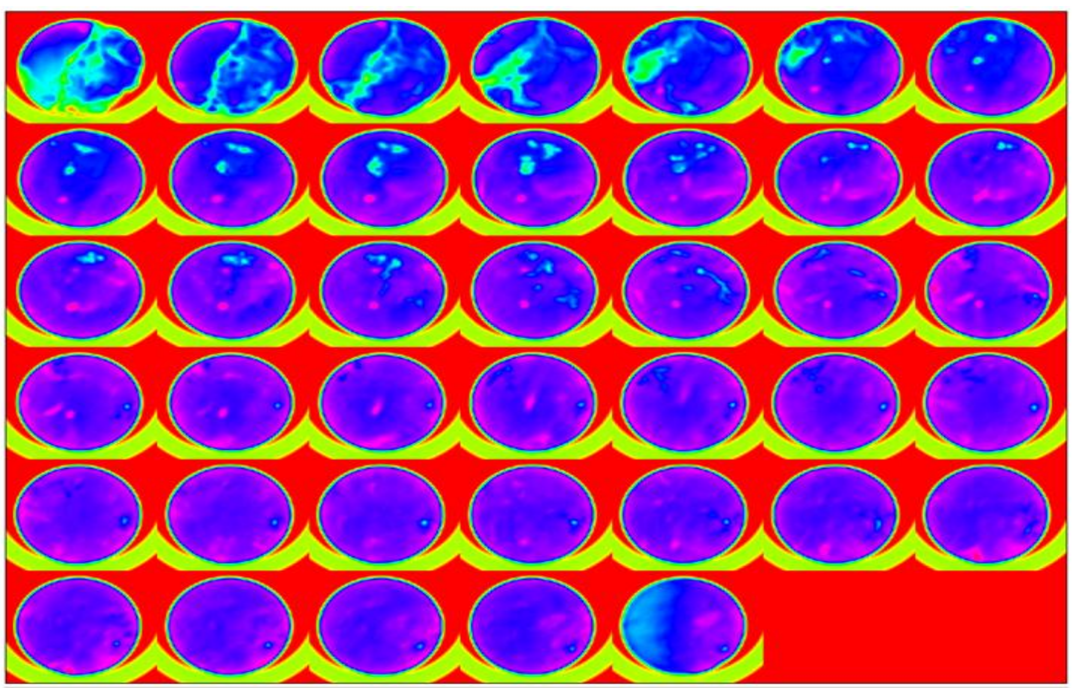

After Acidizing

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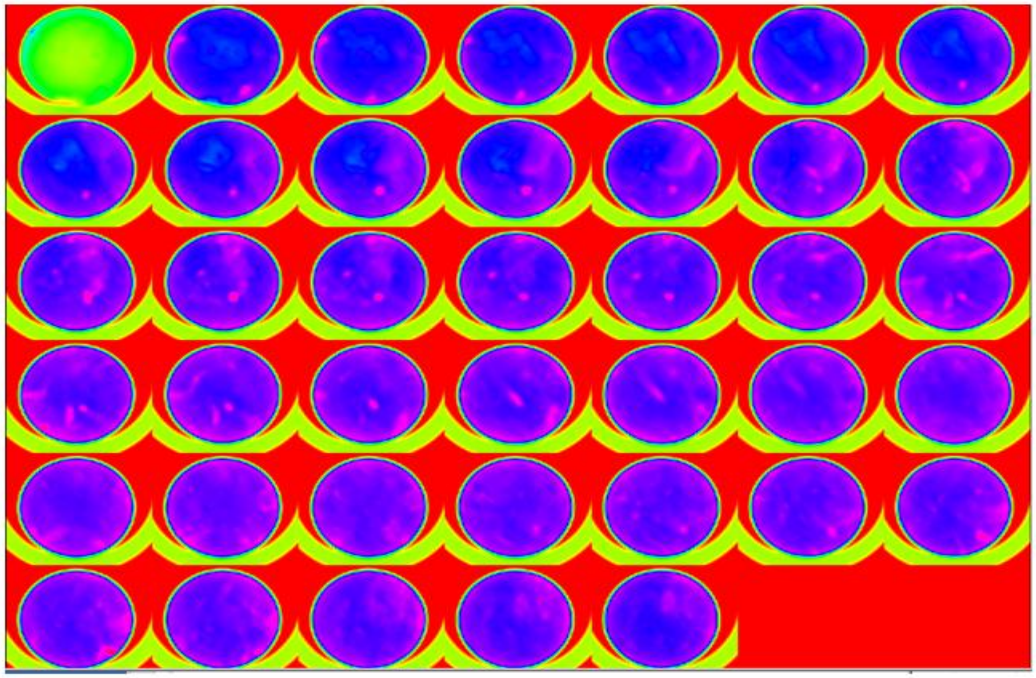

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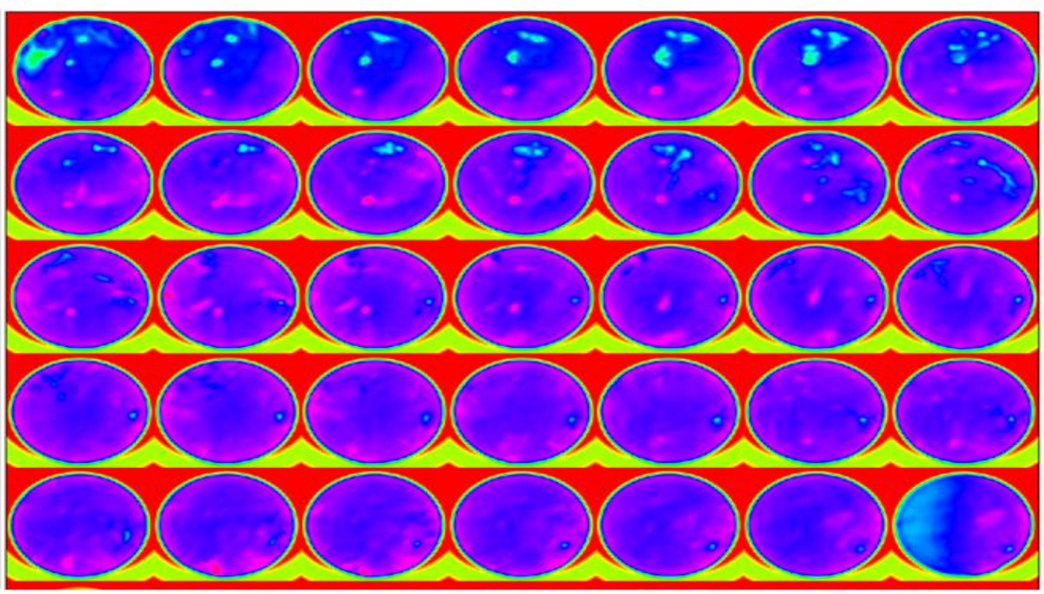
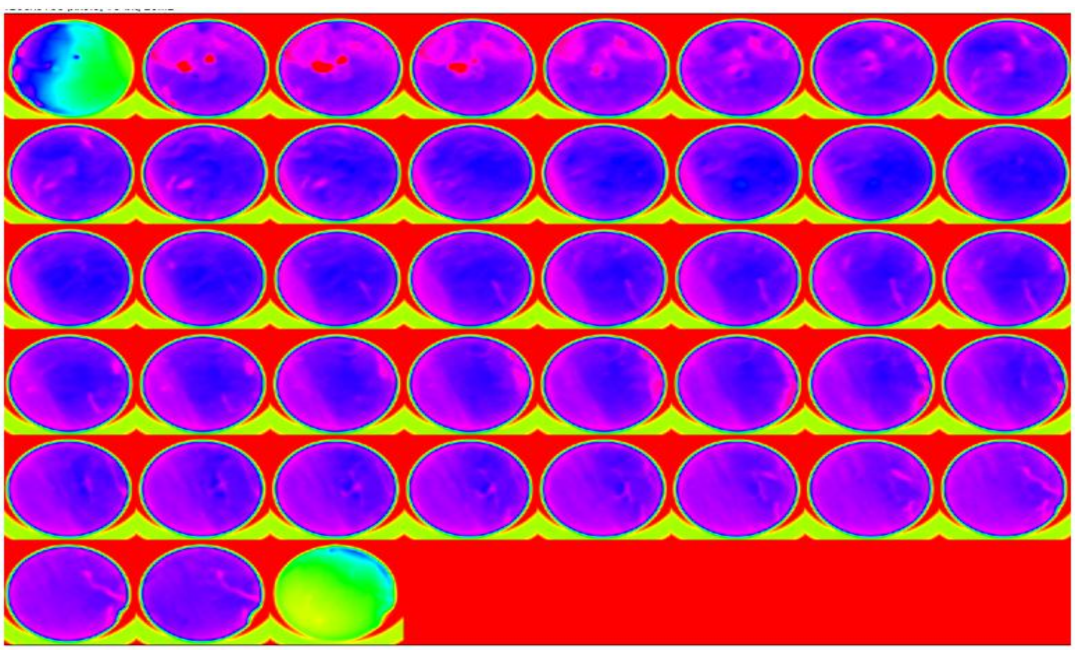


After Acidizing

Core 9



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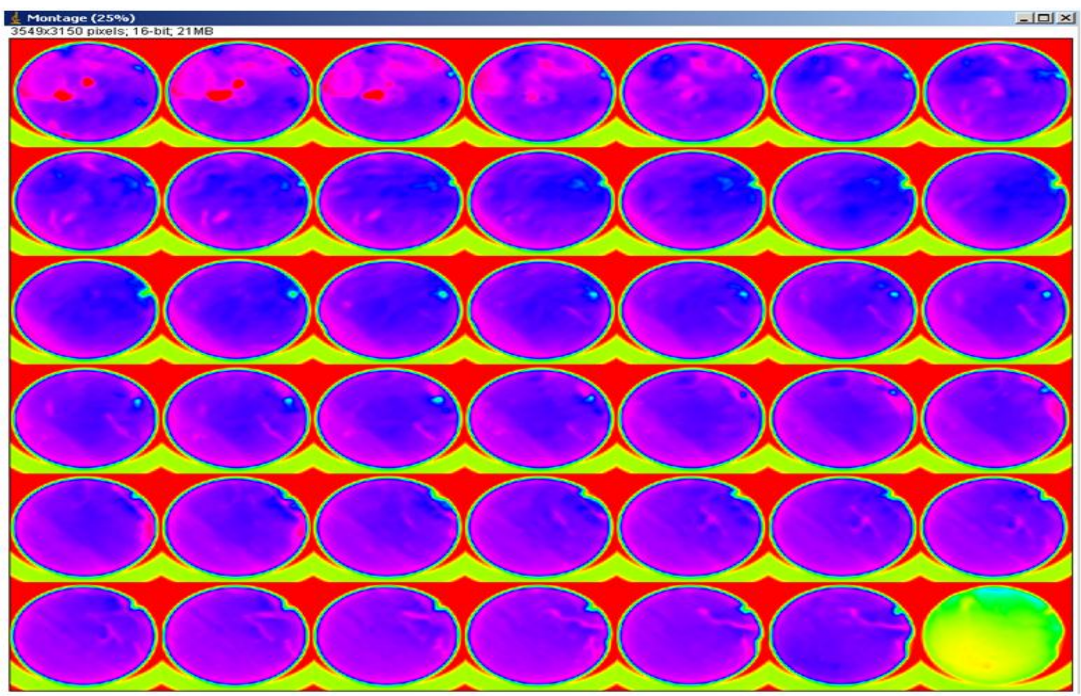
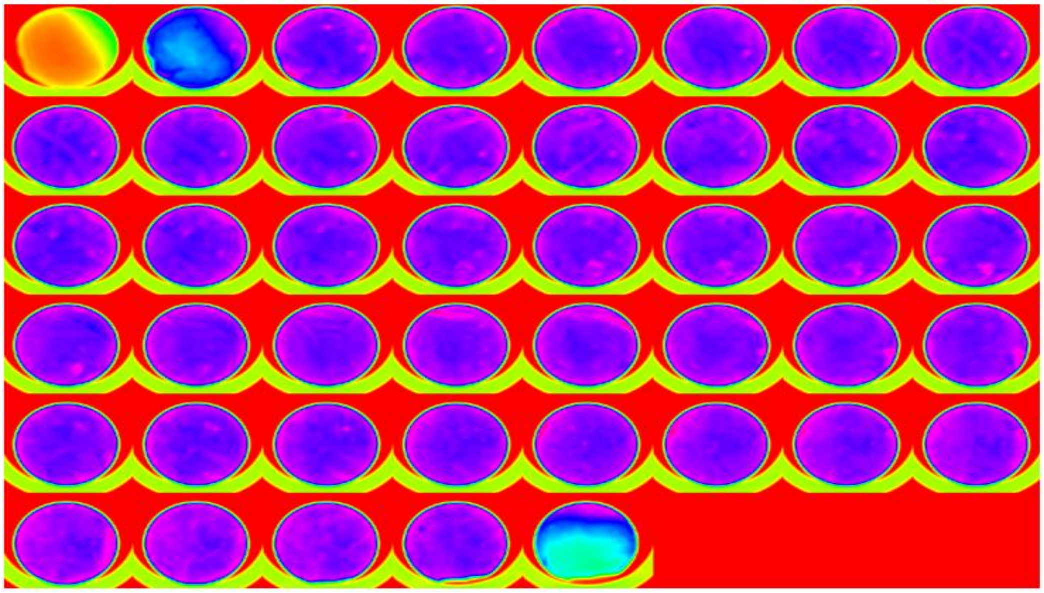


After Acidizing

Core 11



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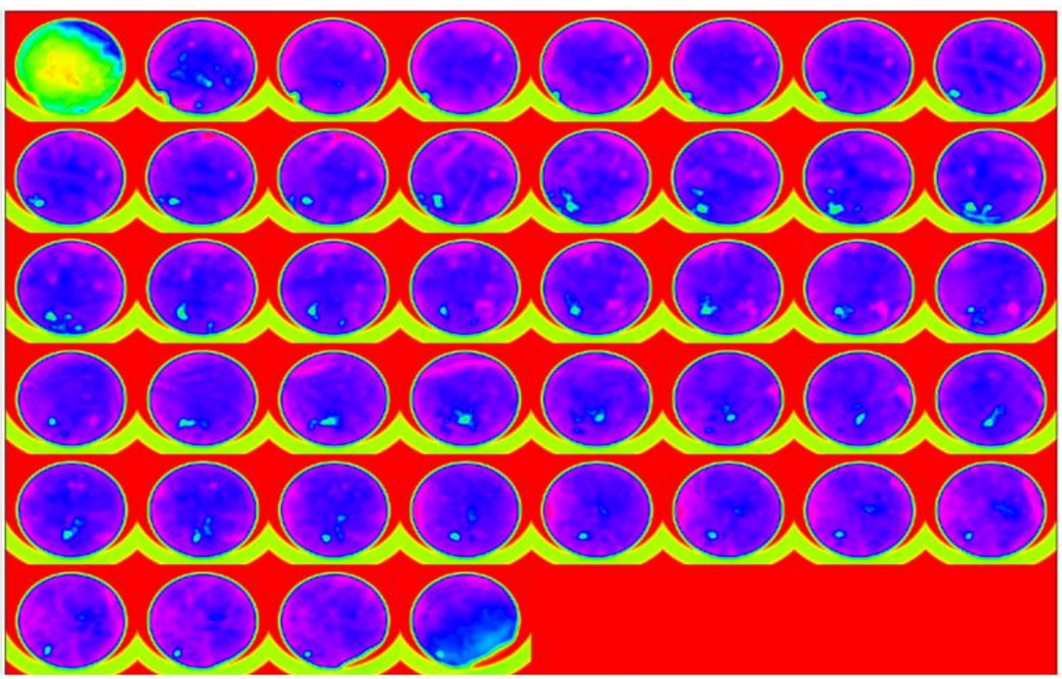

After Acidizing

VITA

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