Improving Sandstone Matrix Stimulation for Oil Wells by Gas Preconditioning

by

Mohammed Ahmed Al-Muhareb

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

November, 1999

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UMI Number: 1398016

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KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, SAUDI ARABIA

COLLEGE OF GRADUATE STUDIES

This thesis, written by **Mr. Mohammed Ahmed AL-Muhareb** under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** in **PETROLEUM ENGINEERING.**

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Dedication

I dedicate this thesis to my loving wife

Acknowledgment

In the name of Allah, Most Gracious, Most Merciful

Acknowledgment is due to the Department of Petroleum Engineering for supporting this thesis and to Saudi Aramco company for giving me the opportunity to peruse my M.S. degree and for supplying the oil samples.

I am greatly indebt to my thesis advisor, Dr. Mohamed A. Aggour for suggesting the research topic and for his constant support and careful supervision during the course of this research. I deeply appreciate the guidance and suggestions provided by other members of the thesis Committee, Dr. Abdulaziz A. AL-Majed, the chairman of the Department of Petroleum Engineering and Dr. Sidqi Abu-khamsin.

I wish to express my appreciation to the supervisor of Petroleum Engineering laboratory, Mr. Mansour M. AL-Dhafeer, and to the laboratory staff, Mr. Abdul-Rahim Muhammadain, Mr. Abukari Iddris, Mr. Abdul-Samad Iddris, Mr. Moussa Ali Moussa, and Mr. Ahmad AL-Shuwaikhat for their help and contribution to the successful completion of the experiments.

Finally, I extend my appreciation to my wife, children and parents for their patience and encouragement.

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ملخص الرسالة

بناءً على المعلومات والمراجع العلمية المختصة بتحفيز آبار الزيت المنتجــة مــن تكوينـات الصخور الرملية , فان الاستجابة من الحامض تبلغ ذروتها عندما تكون كمية الحامض لكل قدم مــن التكوين المعالج قليلة نسبيا وبعد ذلك يبدأ في التزول لمرحلة ما بعد حجم المعالجة المثالي. الســـبب في ذلك أن الزيت الخام الموجود في المنطقة المراد تحفيزها يحد من تحفيز آبار الزيت لأن التفـــاعل بـــين الزيت الخام والحامض المستهلك ينتج عنه ترسبات قادره على سد المسامات وتقليل نفاذية الطبقــــة الصخرية و من ثم إعاقة حركة سريان السوائل. الطريقة المثلى لازالة هذا العائق هو إزالة الزيــت أولا من الطبقة المراد تحفيزها بضخ كمية من الغاز قبل بدء عملية التحفيز.

تمّ اجراء تجارب مخبرية لمعرفة تأثير نتائج التحفيز على عينات من الصخور الرملية من نـــوع "برّيه" (تحت حالات ضغط و حرارة مماثله لحالات مكامن الزيت) وقد تمّ التوصل الى نتائج مهمـــة. هذه التجارب اثبتت أن النفاذية تتحسن لدرجة معينة وثم ما تلبث أن تنخفض عند استخدام كميـلت كبيرة من الحامض (١٢٪حامض الهيدروليك و ٣ ٪ حامض الهيدروفلوريك) لتحفيز آبار الزيت بدون ضخ غاز في المنطقة المراد تحفيزها.

ولكن هذه النتائج تحسنت بشكل مذهل وبصورة طردية عندما تمّ تهيئة هذه العينـــات مـــن الصخور الرملية المراد تحفيزها بازالة الزيت منها بواسطة ضخ غاز النتروجين او غاز ثاني أوكســـيد الكربون. اضافة الى ذلك تبين أن النفاذية تتحسن بصورة أفضل كلما تمّ زيـــادة كميـــة الحــامـض المستخدم في المعالجة. في هذا البحث يتم عرض نتائج هذه التجارب والتي تبين مدى تأثـــير عمليـــة التحفيز بعد تهيئة طبقات الزيت بالغاز.

THESIS ABSTRACT

Full Name of Student :   **Mohammed Ahmed AL-Muhareb**

Title of Study :   **Improving Sandstone Matrix Stimulation for Oil Wells by Gas Preconditioning**

Major Field :   **Petroleum Engineering**

Date of Degree :   **November 1999**

Experience has shown that the response of oil wells to sandstone matrix acidizing is different from the response of gas wells. For oil wells, the improvement in permeability resulting from the stimulation treatment peaks at a certain acid volume and then decreases as the acid volume increases. For gas wells, however, the improvement is roughly proportional to the acid volume. It has been reported that stimulation of oil wells could be improved by displacing the oil in the zone to be acidized by gas. Gas preconditioning is sought to prevent the formation of emulsions or sludges resulting from the reaction between the oil and spent acid products.

The present research investigates the effect of gas preconditioning of the damaged zone on permeability improvement. Experiments were conducted on Berea sandstone cores saturated with 29.2° API oil at selected reservoir conditions of 180° F and 3,000 psi. CO_2 and N_2 gases were used alternatively for preconditioning. It was found that with gas (CO_2 or N_2) preconditioning, improvement in permeability increased with increasing acid volume. Further, using gas preconditioning with small volume of acid, that would be ineffective with regular stimulation, would result in improvement of up to 200% of the original permeability. At an acid volume that would just restore the original permeability, the gas preconditioning would yield about 300% improvement.

It was also found that CO_2 is more effective than N_2, which is expected to be due to the difference miscibilities of the two gases.

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS

DHAHRAN, SAUDI ARABIA

NOVEMBER 1999

Chapter - 1

CHAPTER 1

INTRODUCTION

Matrix acidizing is defined as the injection of acid into the formation below fracturing pressures. The objective of matrix acidizing treatment is to achieve, more or less, radial acid penetration into the formation in order to remove near wellbore damage and restore permeabilty and the ability of the zone to produce effectively.

Basically, there are two causes of impaired productivity, which can be improved by acid treatments:

1) Near wellbore formation damage can cause a well to produce at a rate lower than true reservoir flow capacity. This type of damage is related to a variety of completion and drilling practices such as the loss of drilling and completion fluids, filtrates, or drilling mud particles

2) Low productivity due to low reservoir permeability. Productivity from a sandstone reservoir can be improved through the use of hydraulic fracturing with proppant, a relatively expensive process which is much more extensive than matrix acidizing.

Through the scope of this project, the focus will be on sandstone matrix stimulation and the techniques that could improve such stimulation. Acidizing sandstone formations results primarily in dissolution of acid soluble permeability-damaging minerals rather than in creation of new flow paths, as is the case with acidizing carbonates. Besides the basic quartz grains, sandstones contain other silicoaluminate compounds that are often

located in the pore space and provoke flow restrictions. Sandstones occasionally contain carbonates, metallic oxides, sulfates, sulfides or chlorides, and amorphous silica.

Hydrofluoric acid (HF) is the most common acid used for sandstone acidizing because it is one of the few acids that dissolves siliceous minerals. Therefore, all formulations used in matrix sandstone acidizing typically involve some forms of hydrofluoric acid. The most commonly used system is "mud acid", a mixture of hydrochloric and hydrofluoric acids in variable proportions.

Sandstone matrix stimulation involves the use of hydrofluoric-hydrochloric acid (mud acid) to dissolve sand, clay and other siliceous minerals in a sandstone formation. This matrix acidizing technique restores near wellbore permeability by dissolving minerals and deposts that are blocking the pores of the reservoir rock. Productivity improvement from sandstone acidizing is limited to the removal of near wellbore damage since the permeability is restored in a region extending less than one meter from the wellbore.

Typical sandstone acidizing consists of three stages: (1) a preflush where an aqueous solution of hydrochloric acid is injected to displace resident salt water and to dissolve carbonates that may be present in formation (2) a mud acid stage where an aqueous solution of hydrochloric and hydrofluoric acids is injected to dissolve clays either introduced into the formation or chemically modified by drilling or completion operations and (3) an afterflush stage where an aqueous solution of hydrochloric acid is used both to force the spent mud acid into the formation and to help cleanup products of the acid reaction. Mutual solvents may also be used in the latter stage to facilitate the cleanup process.

Even though mud acid is commonly used in the oil industry to remove near wellbore formation damage in sandstone formations, it still has two limitations to success:

1) Limited penetration of reactive mud acid.
2) Precipitation of dissolved siliceous products.

A previous analysis of field experience by Gidley (1985) [1] observed that in the acidizing of oil wells (unlike gas wells) response peaks at relatively low acid volumes per foot of formation treated, and declines beyond the optimum treating volume. The reason is that the resident crude oil in the area to be acidized reacts with the spent acid products yielding precipitates that are capable of plugging pore spaces and reducing fluid conductivity. In a later study by Gidley et al. (1993) [2], they reported a method for improving acid stimulation for oil wells in sandstone formations. They observed that preconditioning the formation, by displacing oil in the zone to be acidized with CO_2, improves the relative permeability to aqueous acidizing fluids and increases their effectiveness in stimulating the oil zone. No further studies have been conducted on this high potential treatment of damaged oil wells. Therefore, the present research is directed to provide further investigation and evaluation of the effect of gas preconditioning for oil well stimulation by matrix acidizing.

Chapter - 2

CHAPTER 2

Literature Review

Treatment of sandstone formations with acid solutions, particularly mixtures of hydrochloric-hydrofluoric acids, has received considerable attention in the last forty years. This chapter presents a review of the state of the art in this area.

Monaghon et al (1958) [3] investigated the serious reduction in productivity of oil and gas formations during drilling, completion & Workover operations. They noticed from the field behavior that the productivities of certain oil- and gas-bearing formations have been damaged by exposure to drilling muds. This reduction in well productivity, called "formation damage", causes serious consequences. The interaction between water and formation clays reduces permeability of the reservoir rock and that the permeability generally decreases as salinity of the water decreases. They tested some cores in the laboratory and observed the followings:

1. Kaolinite, Illite and Montomorillonite can cause permeability reduction by hydration and migration when contacted by fresh water.

2. Aqueous solution of electrolytes or oil solutions of various organic materials such as amines or alcohols, can partially restore oil permeability of a sand damaged by fresh water.

3. The addition of 1% to 2% of Calcium Chloride and other salts such as potassium and ammonium chloride to fresh water can be effective in preventing formation damage caused by the interaction between clay and fresh water.

Smith et al (1965) [4] showed that on the initial contact of HF with a sandstone core the acid reacts with calcite (CaCO₃) forming a precipitate of calcium fluoride (CaF₂) that reduces permeability. The extent of this reduction was found to be related to the HF concentration of the acid, the low gradient imposed during acid treatment, and the mineralogical composition of the sandstone core. In core experiments, the initial reduction in permeability resulting from acid attack is overcome when enough acid is injected to dissolve plugging materials or to enlarge alternate flow channels. It seems reasonable to expect that in the reservoir, the zone of reduced permeability migrates deeper into the formation with continued acid injection. The effect on well productivity is obviously less as this zone becomes farther from the wellbore. Also, in a highly damaged formation, stimulation occurs only after the zone in which the permeability is reduced (by acid attack) has cleared the damaged zone and pushed deeper into the formation.

A typical sandstone reservoir may contain 50 to 85 per cent silicon dioxide, (i.e. sand, silica or quartz). Silica reacts with HF to yield silicon tetrafluoride (SiF4) as an intermediate product. In the presence of excess HF, the silicon tetrafluoride reacts rapidly to produce fluosilicic acid (H2SiF6) as the final reaction product. This reaction of silica with HF does not occur at a rapid rate; hence, quartz grains dissolve slowly during a sandstone acidizing treatment. The following equations describe the typical reaction of HF acid with silica and silicon tetrafluoride.

$$4\,HF \;+\; SiO2 \;====>>\; SiF4 \;+\; 2H2O \qquad\qquad 2.1$$

2 HF + SiF4 ====>>   **H2SiF6** (Fluosilicic acid)   2.2

Farley et al (1970) [5] investigated the reaction of HCl-HF on sandstone cores at reservoir conditions and concluded the following:

1. Reservoir temperature and pressure are very important variables that contribute to acid spending. Increased temperature is observed to increase the reactivity between HCl-HF and sandstone formation. There are two competing pressure effects. The solubility of by-product gases, carbon dioxide (CO_2) and silicon tetrafluoride (SiF_4), is greater at higher pressure. Increased silicon tetrafluoride solubility enhances the attack on silicate minerals by fluosilicic acid. Thus, the response of a sandstone reservoir to matrix acidizing is very temperature and pressure dependent.

2. Formation competence is changed by acidizing; over treatment may cause grain shifting and possibly formation collapse under overburden stress.

The distribution and type of minerals in a matrix, as well as previously mentioned factors, dictate the composition and volume of acid best suited for that zone.

Gidley (1971) [6] conducted studies on Berea core samples and on real sandstone formations to investigate acid stimulation involving a mutual solvent. He concluded that in stimulating sandstone formation, following the acid treatment by an afterflush of diesel oil containing a mutual solvent such as Ethylene Glycol Monobutyl Ether (EGMBE) assures both fines and formation will be water wet. Field results showed that EGMBE can help in increasing oil productivity several times as much as conventional HF-HCL acid treatments.

Guin et al (1971) [7] developed a mathematical model for predicting the results of matrix acidizing. The essential idea of this work involves computation of the change in the pore-size distribution resulting from the erosion of a microstructure of a porous medium by an acid. The simulation method is very useful for studying matrix acidization. The technique provides an estimation of permeability improvement that will result from the acid treatment of clean sandstone.

Sutton et al (1972) [8] investigated the stabilization of crude oil-acid emulsions by fine solids and the influence of corrosion inhibitors and surfactants. They concluded the following:

1. In the crude oil/acid emulsion system, the wettability of fines was found to be of minor importance in emulsion stability in the presence of non-emulsifying surfactants.

2. The corrosion inhibitors used (acetylenic alcohols,) appeared to have only minor effect on the performance of non-emulsifying surfactants.

3. The adsorption of surfactants by fine can decrease the effectiveness of some demulsifiers.

4. The addition of EGMBE to HF-HCl systems appeared to decrease emulsion stability.

5. In many cases, oil-wetting tendencies of silica surfaces appeared to be stronger in brine than in acid, except when strong water-wetting surfactants were used.

6. Ten per cent EGMBE in acid was found to facilitate desorption of both corrosion inhibitor and surfactants from silica surfaces.

McCune et al (1975) [9] demonstrated a practical method for applying laboratory results with cylindrical cores to the design of acid jobs. As mud acid is injected into the matrix of a sandstone, an acid-mineral reaction zone is developed and moves at a velocity much less than that of the acid itself. As a result, the rock volume stimulated is much smaller than the volume filled by the acid. Laboratory stimulation tests with undamaged sandstone cores showed that, as mud acid was injected at a constant rate, the permeability rose rapidly after a time delay that was correlated with injection rate, HF concentration, and core length.

The authors summarized their observations as follows:

1. Laboratory tests demonstrated the existence of a new permeability front that is formed during acidizing and moves at a velocity proportional to the acid strength and flow rate, but much slower than the velocity of the flowing acid.

2. Solution of the differential mole balances of the HF and dissoluble minerals yielded equations describing the acid and the minerals concentrations as functions of time and position.

3. Given a correlation of permeability vs. porosity, the model may be used to predict the permeability change in a sandstone resulting from acidizing.

4. The model was translated to the radial geometry around the wellbore

5. The radial model clearly demonstrates that as mud acid is injected out from the wellbore, the radius of the zone through which the reaction front passes is much smaller than that filled by the acid.

Hill et al (1981) [10] developed a mathematical model that can predict the depth of acid penetration in sandstone formation. The model uses both the chemical composition of the formation and its pore size distribution. The model predictions showed reasonable agreement with experimental data and yielded specific information about the reaction characteristics of the sandstone HCL/HF system.

Shaughnessy et al (1981) [11] proposed a design criterion based on type and depth of damage in sandstone formation which can replace laboratory design curves that may have been distorted by CO_2 evolution. They reported that silica precipitates from spent acid when the concentration of remaining HF becomes very low. The reaction that dissolves silicate minerals by consuming HF when concentration is high,

$$SiO_2 + 6HF \implies H_2SiF_6 + 2H_2O \qquad 2.3$$

reverses itself to regenerate HF and precipitate silica as the HF concentration drops as follows:

$$H_2SiF_6 + 4H_2O \implies Si(OH)_4 + 6HF \qquad 2.4$$

However, this silica precipitates as a voluminous hydrated colloid $[Si(OH)_4 .nH_2O]$ that is damaging to rock permeability. The best solution to the silica precipitation problem is to produce the spent acid from the well as quickly as possible. They added that since most formations contain iron, it could precipitate from spent acid solutions to yield an amorphous gel. It is important to understand the conditions under which this

precipitation takes place so that acidizing fluids and field practices can be designed correctly.

Muecke (1982) [12] emphasized that only properly designed and implemented acid stimulation treatment would improve the productivity of oil and gas wells. The success of these treatments depends to a great extent upon proper acid selection and good treatment design. This can be accomplished only with a good understanding of the fundamental principles of acid stimulation. Muecke summarized the important principles and reported descriptions of the basic concepts of damage removal, reservoir stimulation, acid reaction mechanisms, job design and diversion technology.

Gidley (1985) [1] conducted a study to determine how the response of sandstone formations is related to the individual components of acid treatments employed on them. Gidley observed that gas wells and oil wells respond differently to the amount of mud acid used in the treatment. With gas wells, in the range of acid volumes examined (from less than 20 to more than 200 gal/ft), the stimulation response was roughly proportional to the amount of mud acid employed. With oil wells, however, the response from the treatment peaked at a certain acid volume (averaging about 75 gallons of acid per foot of formation thickness).

Lea et al (1993) [13] examined the effect of the diverting agent cake on the acidizing efficiency in removing near-perforation damage. Results showed that diversion within a

perforation has little effect on stimulation performance. Their observations were summarized as follows:

1. For acidizing treatments at the perforation level, the diverting agent cake exhibits a dominant influence on flow distribution across the perforation. Flux usually is equalized in the early stages of acid injection.

2. Acid treatment in the formation is affected strongly by the intensity and extent of the existing near-wellbore damage. Fluid diversion caused by a filter cake at the perforation surface may lead to deeper acid penetration in the damaged zone. However, the fluid that enters the damaged zone will be directed toward adjacent zones of higher injectivity because of the higher flow resistance in the damaged region. The effect of a diverting agent on acid propagation into the damaged zone is limited.

3. For a given injection volume, the acid injection rate imposes a similar effect on both the pressure drop across the diverting-agent cake and the pressure drop in the formation. Thus, diverting-agent efficiency or fluid diversion is insensitive to the injection rate.

Suzuki (1993) [14] investigated the detrimental effects of sludge formation during acid stimulation treatments. She observed that some crude oils have strong tendencies to form sludges when the crude is in contact with a strong acid such as 15% HCl, and the conventional anti-sludge additives are ineffective in controlling it. Moreover, the sludging is more severe when iron is present in the acid. The major source of iron is corrosion and mill scales in the tubing. Laboratory observations indicated that sludging

can cause serious plugging in the formation leading to ineffective acidizing. Now with the new families of effective additives, the acid sludging can be controlled economically even in the presence of up to 40,000 ppm iron in very strong acid such as 15 to 28% HCl.

Malekzadeh et al. (1993) [15] investigated the acid stimulation treatments of horizontal wells. They observed that the combined effect of the formation damage and the presence of impermeable barriers and low permeability regions in the vicinity of some sections of the wellbore would make some sections of the horizontal wellbore unproductive. This will manifest itself as a skin factor in well test analysis if the total drilled length of the horizontal section is used in the calculations. Therefore, Malekzadeh et al derived new equations for evaluating the actual length of the horizontal well contributing to production.

Gidley et al (1993) [2] reported a new improved method for acidizing oil wells in sandstone formations. After they conducted labrotaory study and field tests, they concluded that preconditioning the formation by displacing the oil in the zone to be acidized with CO_2 improves the effectiveness of a mud acid treatment and improves the relative permeability to aqueous acidizing. This preconditioning step is thought to eliminate the formation of emulsions or sludges between spent acid products and the crude oil that otherwise would be contacted.

Halliburton (1997) [16] conducted a study to determine the most effective acid system for sandstone formation. Their research revealed a complex reaction process based on

acid concentration, temperature, and the target mineralogy. Based on this research, the Sandstone 2000™ Acid System was developed. They said approximately 90% of the wells treated with the Sandstone 2000 Acid System have been returned to production with a two- to four-fold increase in production rate. A special flowchart was designed to help engineers determine the best acid blend for their needs. Halliburton developed 5 different types of acids. The correct ratio of HCl to HF in an acid blend is selected based on the minerals present in the target area of the well. The Sandstone 2000™ Acid System consists of the following:

1) Sandstone Completion™ Acid
2) Fines Controls™ Acid
3) K-Spar™ Acid
4) Volcanic™ Acid
5) Silica Scale™ Acid

Chapter - 3

CHAPTER 3

STATEMENT OF PROBLEM AND OBJECTIVES

OF THE STUDY

The literature contains much discussion of both the theory and practice of acid stimulation of oil wells in sandstone formations. It has been reported that the resident crude oil in the area to be acidized causes a problem in stimulation of oil wells due to the reactions between the resident crude oil and the spent acid products. Such reactions yield precipitates that are capable of plugging pore spaces and reducing fluid conductivity. Gidley et al [2] have suggested the displacement of resident oil in the zone to be acidized with gas, so that the reactions between the spent acid products and formation fluids are nearly eliminated.

Very limited work has been conducted in this area. With the indicated potential of preconditioning, it needs to be further investigated and evaluated. Therefore, the objective of the present research was to investigate and evaluate the improvement of the oil well stimulation by preconditioning the damaged zone with gas injection. More specifically the objectives of this research is to investigate:

1. The effect of acid volume on permeability improvement without gas preconditioning and thus, determine the optimum acid volume.
2. The effect of gas preconditioning on permeability improvement at various acid volumes.
3. The effect of the type of gas used for preconditioning. For this purpose, CO_2 and N_2 gases were used.

Chapter - 4

CHAPTER 4

EXPERIMENTAL APPARATUS, MATERIALS AND PROCEDURE

4.1   Experimental Apparatus

The experimental apparatus used in the present work is shown schematically in Figures 4.1. It consists mainly of a fluid injection system, gas injection system, high temperature furnace, a core holder, confining pressure hand pump, back pressure regulator, pressure transducers and fluid fraction collection system.

4.1.1   The Fluid Injection System

A two-piston Beckman type pump (model: 100A) was used to inject silicon oil into the transfer cells that are located in the oven. One check valve was fitted at the inlet and another at the outlet of each cylinder to retard back flow when fluids are injected against high pressures. The flow rate was controlled by changing the stroke length on each piston.

4.1.2   The Gas Supply System

Nitrogen and carbon dioxide gases were used respectively in phase-2 and phase-3 of the experiments as described later. Initially, the gas was compressed at high storage pressure of 5000 psi. Then, it was flowed into 25-ft. coil inside the furnace before it enters the core.

A special high-pressure cylinder was used for the displacement process. A high-pressure stainless-steel regulator with high-load needle bearing was used to control the inlet gas

pressure to the core. The regulator was connected to the gas reservoir inlet through ¼-in. stainless-steel tubing.

4.1.3 High Temperature Furnace

A Memmert Carl-Kolp type high temperature furnace was used to house the core holder, fluid transfer cells and the gas heating coil. The oven temperature was maintained at 180 F to simulate reservoir temperature. High accuracy portable thermostat was placed inside the furnace to read the furnace temperature and to check against the built-in thermostat temperature.

4.1.4 Core Holder

Stainless steel Ruska type core holder was used in the experiments with 1 in. ID and 6 in.-long rubber sleeve.

4.1.5 Fluid Supply System

Four high-pressure stainless-steel transfer cells were used for supplying the various fluids to the core. Teflon pistons were used in the transfer cells supplying brine, mud, and oil whereas a stainless-steel piston was used for cell supplying the acid.

4.1.6 Hand Pump

Hand pump (Core Lab. model # 3020-008) was used to provide the confining pressure on the rubber sleeve around the core in the core holder. The confining pressure was set at 4000 psi.

4.1.7 Back Pressure Regulator

Back-pressure regulator (Core Lab, model #: 3600-239) was used to hold 3000 psig back pressure on the outlet of the core holder to simulate the formation pore pressure in the reservoir.

4.1.8 Pressure Transducers

Validyne type high-accuracy digital pressure transducer (model # CD23A-1-C-1-D) was used to measure pressure drop across the core. Two pressure transducers were used. One for low differential pressure measurement before damage. The other one is for high differential pressure measurement usually after damage.

4.1.9 Liquid Fraction Collection System

The produced liquid was collected in 10-ml graduated tubes, which are placed in the fluid fraction collection system (Retriever-II, model: ISCO 34790-0007).

4.2 Materials

4.2.1 Core Plugs

A total of 40 Berea sandstone core plugs were used in the experiments. The average properties of the core plugs are given below while the individual core properties are listed in table 4.1

Length: 10.0 cm
Diameter: 2.51 cm
Pore volume: 11.7 cc
Porosity: 23.0 %

4.2.2 Crude Oil

Medium type crude oil with 29.2 API gravity and 5.3 cp viscosity at 3000 psig and 180 F was used in all experiments.

4.2.3 Brine

2 % KCl in distilled water was used as brine

4.2.4 Hydrochloric/ Hydrofluoric acid (mud acid)

12% HCl – 3% HF mud acid was used in all stimulation experiments.

4.2.5 Mud

The mud used in experiments to create formation damage in the core plugs was prepared in the laboratories from Bentonite and fresh water. The mud density was 64 pcf.

4.3   Experimental Procedure and Calculation

Experiments were conducted on 40 core plugs.

4.3.1   Experimental Procedure

12" x 1" Berea sandstone core is usually cut into three 4" x 1" core plugs. Then, the properties of the core plugs such as diameter, length, area, pore volume, and porosity are then measured. After measuring the core basic data that are needed in permeability calculation later on, the core will be placed inside the rubber sleeve and put in the core holder. The core holder is connected to the rest of the setup as shown in Figure 4.1. Silicon oil is used to provide confining pressure around the rubber sleeve. 2% KCl brine is then injected into the core plug through core end labeled A (Fig. 4.1) to measure the

water absolute permeability at room conditions and reservoir conditions. Then crude is injected into the core through the same core end labeled A to measure the effective oil permeability at reservoir conditions. The mud is then injected through the core to create damage. Oil is then injected into the core to measure the effective oil permeability after damage. Then mud acid (12%HCl & 3% HF) is injected into the core at reservoir conditions to remove the formation damage. Finally, oil is injected into the core at reservoir conditions to measure the effective oil permeability after stimulation. This procedure was repeated for different acid volumes on different core plugs in order to determine the effect of acid volume on oil permeability. This phase of experiments (Phase 1) provided the base data.

However, in phase-2 and 3, preconditioning gas was injected prior to acidizing to investigate its effect on acid treatment.

The general procedure followed throughout the experiments involved the following steps

1. Preparing the set-up.
2. Saturate the clean Berea sandstone with brine and measure the absolute water permeability at room conditions and at reservoir conditions.
3. Displace the brine in the core with oil at reservoir conditions and determine the effective oil permeability.
4. Inject mud into the core at differential pressure of 300-500 psi higher than the back pressure (usually 3-4 cc of mud will create enough damage).
5. Flow oil into the core to measure the effective oil permeability after damage.
6. Stimulate the core with mud acid (HCL & HF) at different acid volume.
7. Determine the post stimulation permeability at different acid volume.
8. Establish the relationship between the permeability improvement and the acid volume.

9. After establishing a base study, the above procedure was repeated with gas preconditioning prior to the mud acid injection step. Nitrogen gas was used in phase-2 while carbon dioxide gas was used for phase-3. Seventy-five pore volumes of gas were found to be the minimum volume required.

10. Determine the effect of gas preconditioning on the improvement of acid stimulation

4.3.2 Calculation procedures

To determine the effective oil permeability at any stage, oil was injected into the core at a constant rate. After reaching steady state, the oil flow rate and the pressure drop were measured. This was repeated at three flow rates of 1, 2 and 3 cc/min. The permeability was calculated from the following equation.

$$k_o = 245 \ q \ \mu \ L \ / (\Delta P \times A) \qquad 4.1$$

Where q = Fluid rate (cc/min)

μ = Fluid Viscosity, cp

L = Length, cm

ΔP = Pressure drop, psi

A = Area, cm2 = $\pi \ (Dia/4)^2$
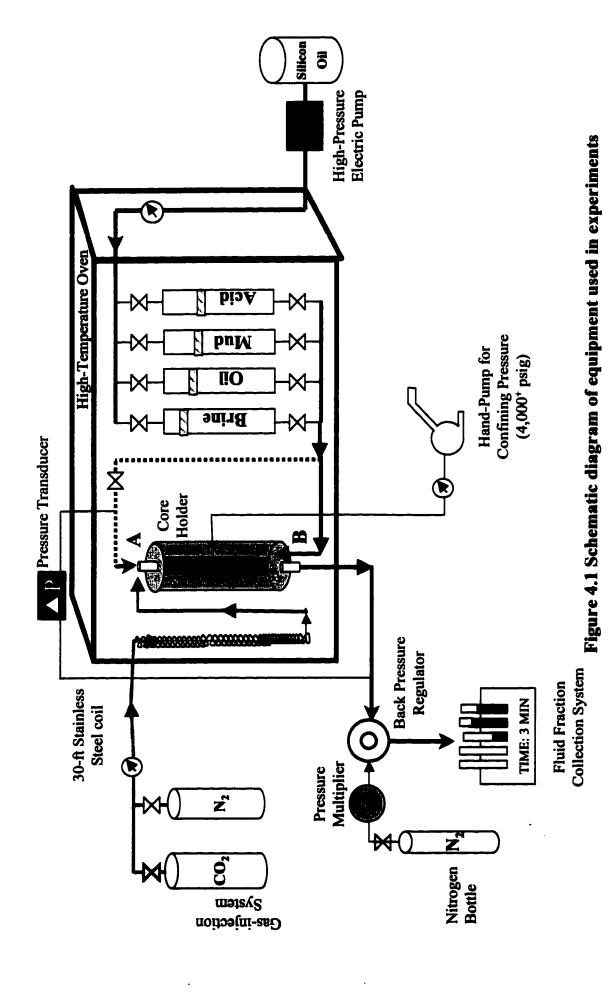
245 = Conversion factor =(14.7 / 60) x 1000

Figure 4.1 Schematic diagram of equipment used in experiments

Table 4.1 Basic core data measurements for all phases

		CORE DATA				
PHASE NUMBER	CORE NUMBER	DIA. (CM)	L (CM)	AREA (CM2)	P.V. (CM3)	POROSITY %
PHASE-1	M-5	2.510	9.945	4.9480	11.698	23.74
	M-7	2.525	9.895	5.0074	11.753	23.68
	M-8	2.525	10.185	5.0074	11.946	23.40
	M-13	2.510	10.065	4.9481	11.548	23.20
	M-14	2.510	10.025	4.9481	11.700	23.60
PHASE-2	M-19	2.520	10.085	4.9876	11.465	22.80
	M-25	2.515	9.705	4.9680	9.530	19.80
	M-26	2.515	10.015	4.9680	9.701	19.50
	M-33	2.510	9.950	4.9480	11.455	23.30
	M-34	2.510	10.070	4.9480	11.427	22.90
PHASE-3	M-35	2.510	10.100	4.9480	11.434	22.90
	M-36	2.515	10.000	4.9680	10.892	21.90
	M-37	2.515	10.020	4.9680	10.850	21.80
	M-38	2.515	10.015	4.9680	11.049	23.20
	M-39	2.510	10.045	4.9480	11.575	23.30
	M-40	2.510	9.945	4.9480	11.361	23.10

Chapter - 5

CHAPTER 5

RESULTS AND DISCUSSION

As mentioned in Chapter 3, the objective of this study was to experimentally investigate and evaluate the improvement of oil well stimulation by preconditioning the damaged zones with gas injection. Accordingly, acid stimulation experiments were conducted in three different phases. Phase-1 is the basis of all experiments where the optimum acid volumes that produce the highest response in permeability improvement without gas preconditioning were determined. Phase-2 and phase-3 of the experiments involved gas preconditioning prior to stimulation. Nitrogen gas was used in phase-2, while CO_2 was used in phase-3.

5.1   Results of Phase-1

Acid Stimulation Without Gas Preconditioning

Different acid volumes were used for this phase of the experiments to investigate the effect of acid volume on permeability restoration/ improvement without gas preconditioning. Fourteen core plugs were used in this phase. Some core plugs failed during experiments due to different reasons such as failure in rubber sleeve, valves, flow lines, or core. Results of phase-1 are summarized in Table 5.1. Figures 5.1 to 5.7 present the permeability measurements at three different conditions, before mud damage, after mud damage and after acid treatment. It can be seen from Table 5.1 and Fig. 5.1 to 5.7 that when using 50, 75, 100, 150, 235 and 320 pore volumes of acid, the percent recovery/ improvement in the original effective oil permeability were 25%, 46%, 65%,

101%, 144%, and 104%, respectively. As the acid volume increased, the restoration in permeability was increased to certain level and then decreased. Figure 5.8 shows the restoration in permeability peaked at 235 pore volumes of acid. The restoration in permeability decreased from 144% of the original permeability when using 235 pore volumes of acid to 104% when using 320 pore volumes of acid.

The decrease in permeability was attributed to the characteristic of oil itself. Crude oil, which is composed of materials having a high molecular weight, has a great tendency to adsorb on precipitates from the mud acid reaction. These precipitates are finely divided colloidal materials of high surface area. When the precipitates occur in the presence of crude oil, some of the components of the crude doubtlessly are adsorbed on the newly developed surfaces thereby altering what should have been a water-wet surface and making it partially oil wet. Initially, the particles in these precipitates are small enough to create solids-stabilized emulsion or sludges, either of which is capable of plugging pore spaces and reducing fluid conductivity.

In summary, the decrease in permeability was mainly attributed to the presence of oil in the area during acid stimulation. If oil is temporary removed from the area to be acidized during stimulation, the acid stimulation response should be proportional to the amount of mud acid employed.

5.2 Results of phase-2

Acid Stimulation with "N₂" Gas Preconditioning

Phase-2 is the second series of experiments where the effect of gas preconditioning on permeability restoration/ improvement at different acid volumes was studied. Under the

assumption that crude oil in the formation being acidized creates the problem, displacement of crude oil from the zone to be acidized seems essential. Nitrogen gas was selected because it is non-flammable and therefore less hazardous than hydrocarbon gases, it is widely available within the well servicing industry, relatively inexpensive, and non-toxic. Therefore it is attractive from the standpoint of personnel safety, economy, and availability.

Table 5.2 and Figs 5.9 to 5.13 summarize the results obtained in phase-2. Four acid volumes were selected. These are 100, 150, 235, and 320-pore volumes acid. It can be seen from Table 5.2 that when using 100, 150, 235 and 320 pore volumes of acid, the permeability improvements were 122%, 143%, 249% and 323%, respectively. The results plotted in Fig. 5.14 show that the response from acid stimulation is roughly proportional to the amount of acid employed. The effect of gas volume injected on permeability improvement was also tested. In Table 5.2, for core number M-25 and M-26, equal acid pore volumes of 150 were used for the two experiments, but 100 and 200 pore volumes of gas were used for preconditioning, respectively. The improvements in permeability were 142.9% for M-25 and 143.8% for M-26. The permeability improvements were almost the same. Therefore, it could be concluded that the gas volume injected is not likely an important factor.

Comparing the results of phase-2 to phase-1 for 100 and 235 pore volumes of acid, it can be seen that the permeability restoration with gas preconditioning is almost twice that without gas preconditioning. Moreover, for the 320 pore volumes of acid, the permeability improvement with N_2 preconditioning was more than three times that

obtained without gas preconditioning. Nitrogen gas injection prior to acid stimulation played a very important role in the permeability improvement.

In summary, preconditioning the sandstone formation, by displacing the oil from the zone to be acidized with N_2 gas, improves the effectiveness of a mud acid treatment. This preconditioning step is thought to eliminate the formation of emulsions or sludges between spent acid products and the crude oil that otherwise would be contacted.

5.3   Results of phase-3

Acid Stimulation With "CO2" Gas Preconditioning

In this phase of the experiments, carbon dioxide was used instead of nitrogen. Results of phase-3 are summarized in Table 5.3 and presented in fig. 5.15 to 5.20.

The acid pore volumes used in phase-3 were 100, 150, 235, and 320. Whereas the gas pore volumes were 75 and 100. Table 5.3 showed that when using 100, 150, 235, and 320 pore volumes of acid, the average permeability improvements were 200%, 295%, 330%, and 381%, respectively. Results plotted in Fig. 5.21 show that the response from acid stimulation in this phase is proportional to the amount of acid employed.

The carbon dioxide preconditioner appeared to have two benefits in modifying the response of stimulation with mud acid. The first was the relative permeability improvement within the oil zone to aqueous acidizing fluids. This made acid penetration of the zone easier. The second benefit was elimination of any interaction between crude oil and acid byproducts. This removed the possibility of emulsion or sludge formation within the zone acidized and provided better treatment response.

5.4   Effect of Mud Acid Volumes

The effect of the volume of mud acid injected for each core plug is shown in Tables 5.1, 5.2 and 5.3. The results on core plugs in phase-1, without gas injection, indicate that the average oil effective permeability appears to reach a maximum with an acid volume of 235 pore volumes. Whereas the results on core plugs in phase-2 & 3 with gas injection prior to acid treatment indicate that the average increase in the oil effective permeability is roughly proportional to the amount of the acid injected.

5.5   Effect of Gas Preconditioning on Acid Treatment

It has been mentioned in a previous analysis of field experience by Gidley [15] that in the acidization of oil wells, response peaks at a relatively low acid volumes per foot of formation treated, and declines beyond that optimum treating volume. However, for gas wells, the stimulation response was roughly proportional to the amount of mud acid injected.

One way of making oil wells respond to acid treatment similar to gas wells is to create an environment similar to gas wells. One method of removing this barrier is to remove the oil from the zone to be acidized and replace it with gas so that the reactions between the spent acid products and formation fluids are similar to those found in a gas zone.

The gas preconditioner appeared to have two benefits in modifying the response of stimulation with mud acid:

1) The improvement of relative permeability to aqueous acidizing fluids within the oil zone.

2) Elimination of any interaction between crude oil and acid byproducts, removing the possibility of emulsion or sludge formation within the zone to be acidized and provide better treatment response.

Therefore, when N_2 gas or CO_2 gas were used in phase-2 and phase-3 respectively, the stimulation response was proportional to the amount of mud acid employed. Unlike the acid response observed in phase-1 where the response from acid treatment peaked at 235 pore volumes of acid. The preconditioning gas has played very important role in the treatment and improved the acid treatment significantly.

It has been proven in phase-3 that CO_2 gas is more efficient than N_2 gas, which was used in phase-2. The reason is that the miscibility of the CO_2 gas is much better than that of N_2 gas. Miscibility pressure for CO_2 is significantly lower than the pressure for the Nitrogen gas, which give CO_2 a major advantage.

5.6 Effect of Gas Type

Two different gases were used as preconditioning gases in this study. Nitrogen gas was used in phase-2 and carbon dioxide gas was used in phase-3. According to the results for phase-2 and 3, summarized in Table 5.2 and 5.3, CO_2 gas is more effective than N_2 gas. The reason is that the miscibility of the CO_2 gas is much better than for N_2 gas. Miscibility pressure for CO_2 is significantly lower than the pressure for the Nitrogen gas, which give CO_2 a major advantage in displacing the oil away from the zone to be stimulated.

5.6.1 N_2 — Miscible Process

For some high-pressure oil reservoirs, N_2 gas may be suitable for achieving miscibility conditions. This gas is particularly attractive because of the ease with which it can be handled and the potential it offers for establishing gravity-stabilized displacement in thick oil columns. Theoretically, nitrogen would be available almost worldwide, but the pressure required for nitrogen to become miscible with crude oils is quite high. There are very few measurements of nitrogen MMP reported in the literature. Most of the data for nitrogen MMP involved relatively light oils with high methane concentrations (30 to 60 moles) and low C_{7+} mole weights.

Sebastian et al [17] conducted a experimental study and reached the following results:

1. The nitrogen MMP for oil goes through maximum with temperature and the maximum is dependent on oil composition.

2. The nitrogen MMP increases as the C7+ mole weight of oil increases.

3. The nitrogen MMP decreases as the methane intermediate concentration of oil.

The following equation was developed in order to predict the nitrogen MMP

$$MMP = 4603 - 3283 * (CL * T / MW) + 4.776 * (CL^2 * T^2 / MW)$$
$$- 4.008 * (CI * T^2 / MW) + (2.05 * MW) + (7.541 * T)$$

Where:

CL : mol fraction of methane in the oil

CI : mol fraction of intermediates (C_2 through C_6 and CO_2) in the oil

T : reservoir temperature in Rankine

MW: mol weight of the C_7 fraction of the oil

5.6.2 CO_2 – Miscible Process

CO_2 is not first-contact miscible with reservoir oils at realistically reachable reservoir pressures. However, past research shows that at sufficiently high pressure CO_2 achieves dynamic miscibility with many reservoir oils. According to the phase behavior concepts, CO_2 vaporizes or extracts hydrocarbons from the crude as heavy as the gasoline and gas/oil fractions. Vaporization occurs at temperatures where the fluid at the displacement front is a CO_2-rich gas, and extraction occurs at temperatures where the fluid at the displacement front is a CO_2-rich liquid. According to the pseudo ternary diagram concept of CO_2 / reservoir oil phase behavior, vaporization/extraction can proceed to such an extent and so alter the composition of displacement fluid at the displacement front that dynamic miscibility results after sufficient contacting has occurred between the CO_2 and the reservoir oil.

The pressure required for achieving dynamic miscibility with CO_2 is usually significantly lower than the pressure required for dynamic miscibility with either natural gas, flue gas, or nitrogen gas. This is a major advantage of the CO_2 miscible process because dynamic miscibility can be achieved at attainable pressures in a broad spectrum of reservoirs.

A disadvantage of CO_2 flooding compared with water flooding results from the low viscosity of CO_2 relative to oil. For example, at a reservoir temperature of 110 F, CO_2 viscosity is about 0.03 cp at 1500 psi, whereas at 2500 psi, the viscosity is about 0.06 cp.

The low viscosity of CO_2 causes the mobility ratio in most CO_2 floods to be unfavorable. CO_2 density is similar to that of oil in many reservoirs, which minimizes CO_2/oil segregation, but there is enough density contrast with brine for gravity segregation to occur when there is mobile reservoir brine.

Despite its low viscosity, CO_2 can be an attractive injection fluid. Dynamic miscibility can be achieved in many reservoirs because of relatively low operating pressure requirement.

Estimation of CO_2 Miscibility Pressure

Yelling et al (1980) [18] conducted experiments to determine the effect of oil composition and temperature on MMP. They varied the relative amount of a light fraction ($C_1 + CO_2 + N_2$), an intermediate fraction (C_{2-6}), and heavy fraction (C_7+) in the oil but maintain the same ratio of one component to another within each fraction with the exception of one oil. They found only a negligible to a small effect of the light to intermediate-molecular-weight materials in the oil on MMP. Their published experiments did not test the effect of a variation in C_7+ properties on MMP, but by correlating MMP vs. temperature only had subsequent predicting with this correlation the miscibility pressure for other oils that had been tested in a slim-tube miscibility pressure apparatus and that represented a significant variation of C_7+ properties, they conducted that C_7+ properties had a minor effect.

Yelling et. al. developed correlation for estimating MMP. Fig. 5.23 shows the correlation for MMP prediction where reservoir temperature is the only affecting miscibility pressure. Whenever Fig. 5.23 predicts miscibility pressure to occur below the

oil bubble point pressure, miscibility pressure should be set equal to the bubble-point pressure.

Holm et al [19, 20] recommended correlation in which both oil composition and reservoir temperature are correlating parameters. The Holm et al method, as extended by Mungan (1981) [21] is shown in Fig. 5.24. According to this correlation,the effect of oil composition on MMP is not large at temperature as low as 100 F, but the effect of oil composition becomes more pronounced as temperature increases above the 120 to 140 F range. This correlation projects an almost asymptotic increase in MMP with temperature for oils with C5+ molecular weight of about 240 or higher.

Table 5.1 Results of oil permeability measurements for phase-1

CORE	PORE VOLUMES		EFFECTIVE OIL PERMEABILITY (MD)			RESTOR 'N
NUMBER	ACID	GAS	BEFORE- DAM	AFTER-DAM	AFTER-ACID	%
M-5	25	0	204	45	69	33.8
M-7	50	0	202	23	51	25.2
M-8	75	0	204	50	93	45.6
M-13	100	0	484	135	315	65.1
M-14A	150	0	475	50	478	100.6
M-14B	235	0	475	50	682	143.6
M-14C	320	0	475	50	495	104.2

Table 5.2 Results of oil permeability measurements for phase-2

CORE	PORE VOLUMES		EFFECTIVE OIL PERMEABILITY (MD)			RESTOR 'N
NUMBER	ACID	GAS	BEFORE- DAM	AFTER-DAM	AFTER-ACID	%
M-19	100	100	200	100	244	122.0
M-25	150	100	315	120	450	142.9
M-26	150	200	320	118	460	143.8
M-33	235	75	550	180	1370	249.1
M-34	320	75	550	140	1778	323.3

Table 5.3 Results of oil permeability measurements for phase-3

CORE	PORE VOLUMES		EFFECTIVE OIL PERMEABILITY (MD)			RESTOR 'N
NUMBER	ACID	GAS	BEFORE- DAM	AFTER-DAM	AFTER-ACID	%
M-35	320	75	550	170	2100	381.8
M-36	235	75	500	135	1650	330.0
M-37	150	100	500	143	1450	290.0
M-38	100	125	550	115	1100	200.0
M-39	150	75	500	180	1500	300.0
M-40	100	75	500	120	1000	200.0
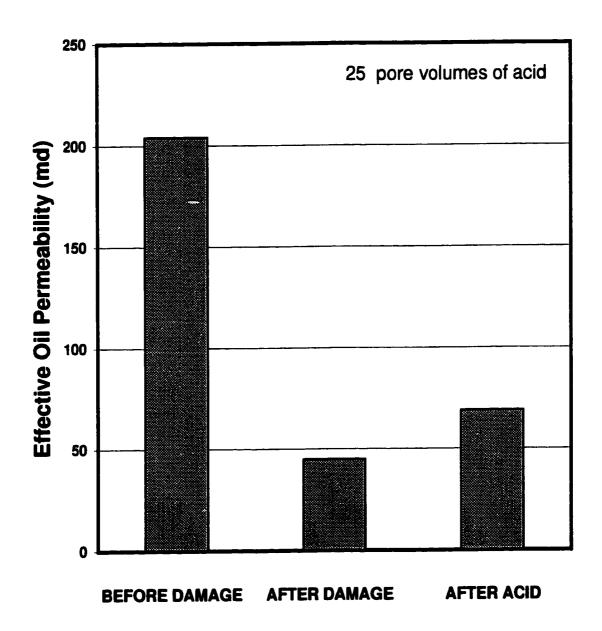
Figure 5.1 Permeability measurement for core M-5
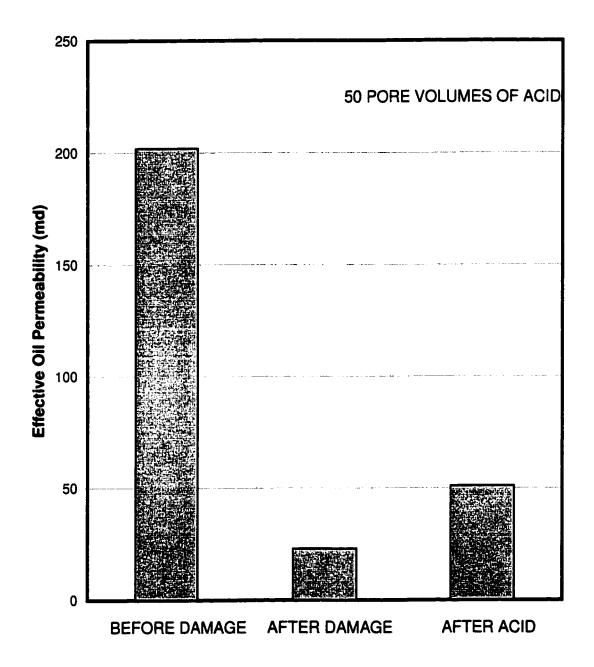
Figure 5.2 Permeability measurement for core M-7
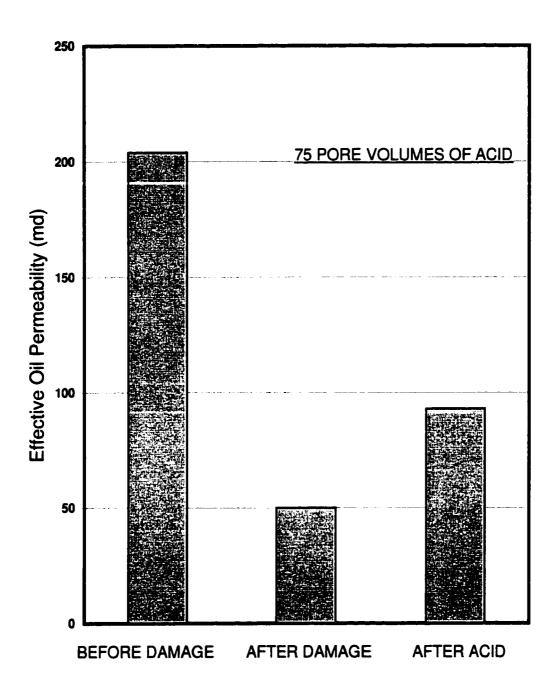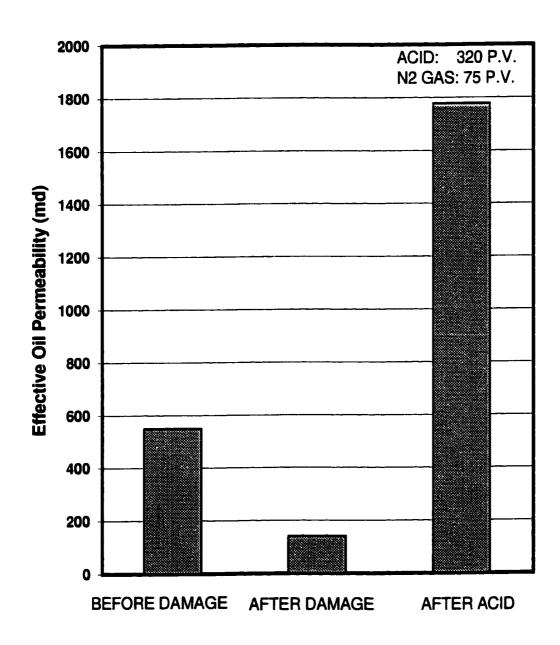
Figure 5.3 Permeability measurement for core M-8
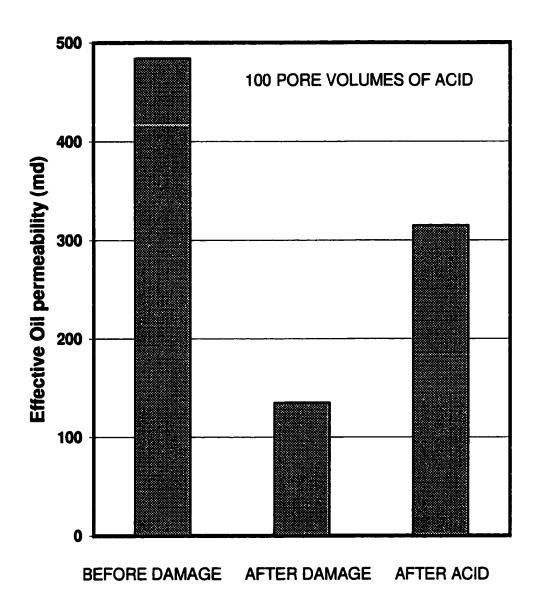
Figure 5.4 Permeability measurement for core M-13
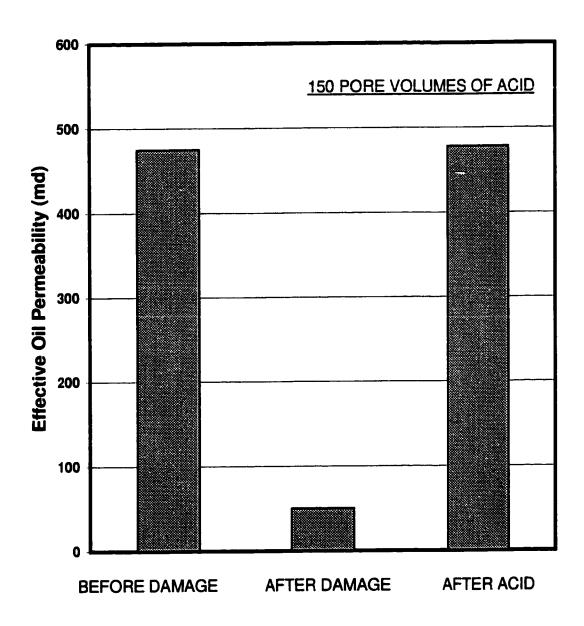
Figure 5.5 Permeability measurement for core M-14A
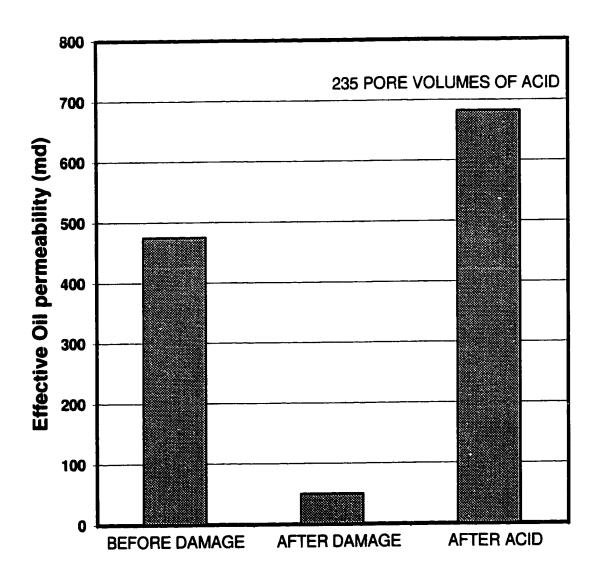
Figure 5.6 Permeability measurement for core M-14B
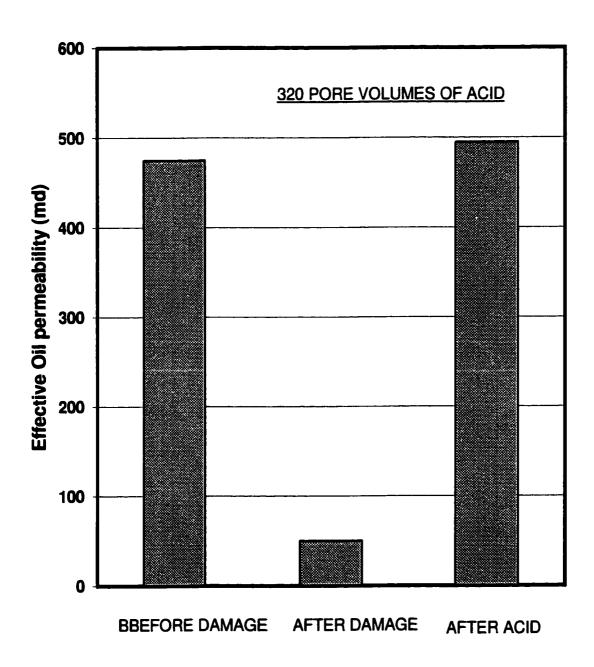
Figure 5.7 Permeability measurement for core M-14C
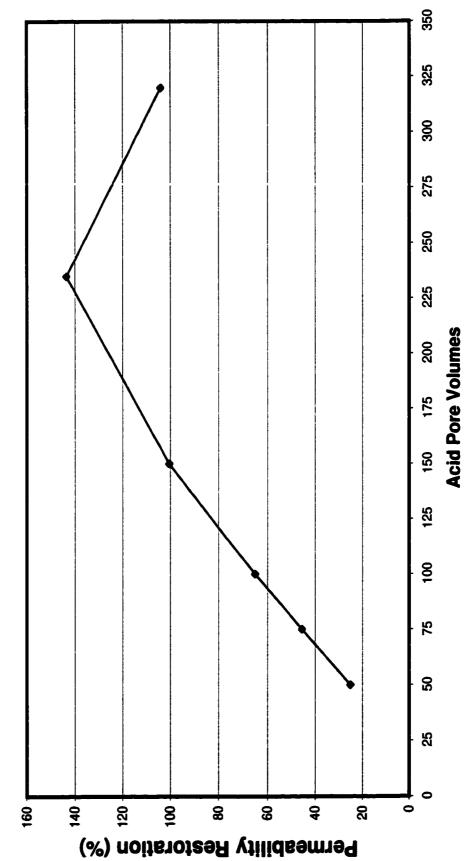
Figure 5.8 Results of permeability restoration vs mud acid volumes for phase-1
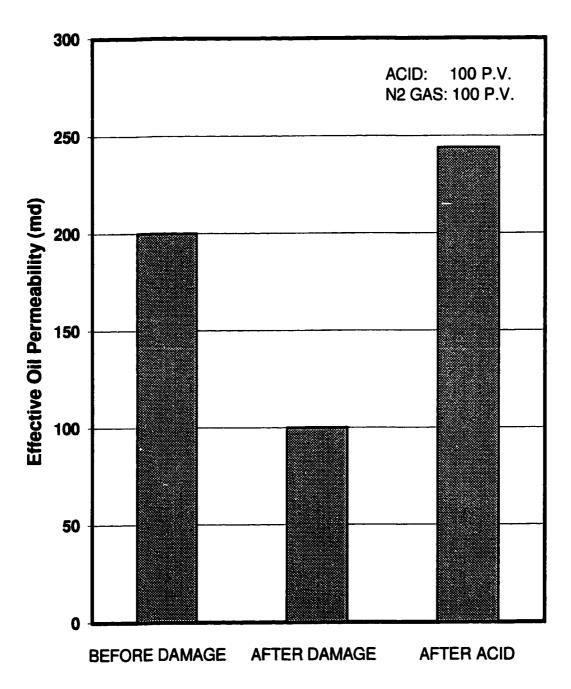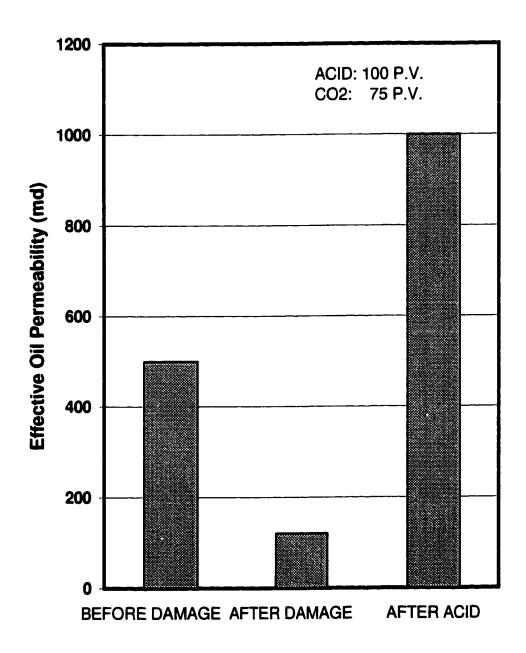
Figure 5.9 Permeability measurement for core M-19
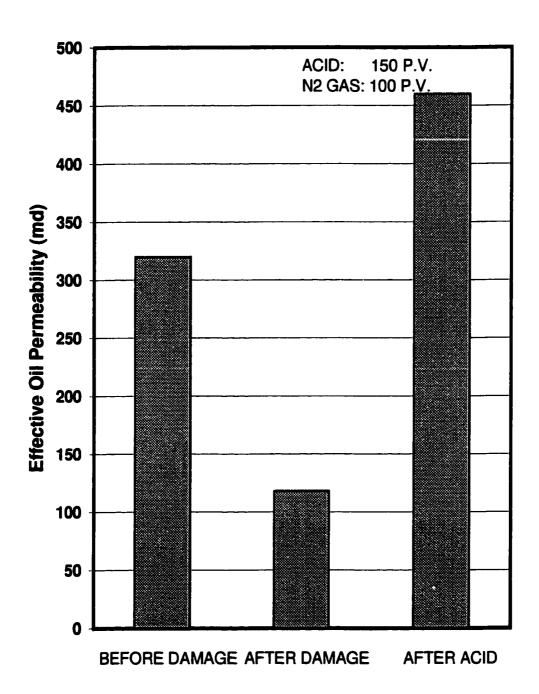
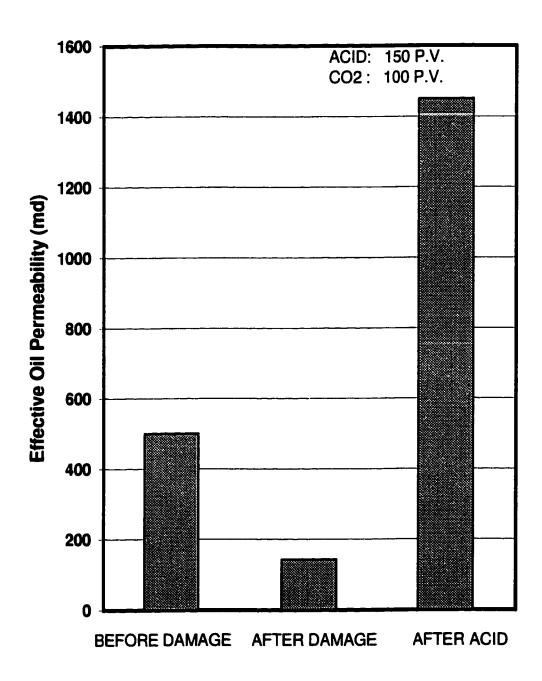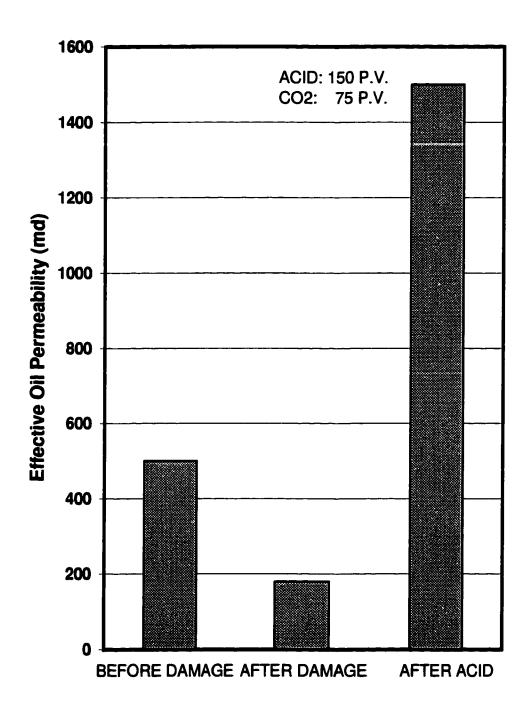**Figure 5.10 Permeability measurement for core M-25**
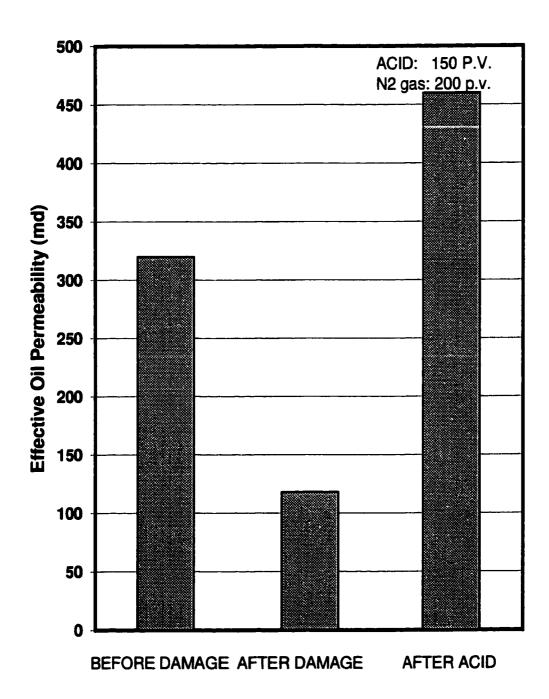
Figure 5.11 Permeability measurement for core M-26
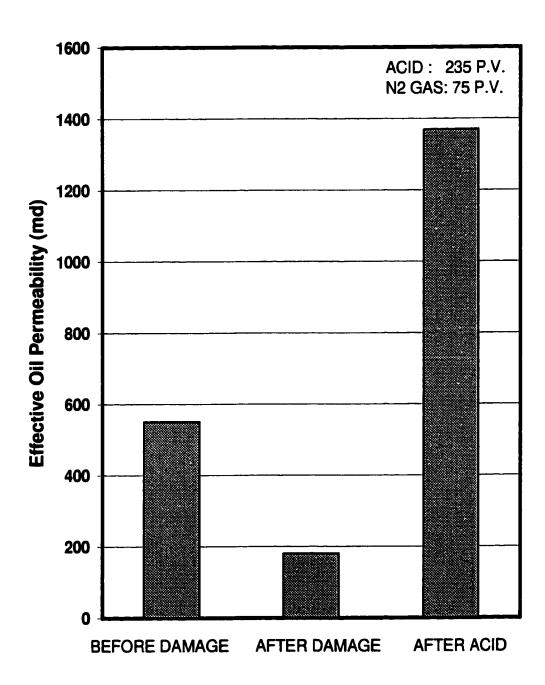
Figure 5.12 Permeability measurement for core M-33

Figure 5.13 Permeability measurement for core M-34
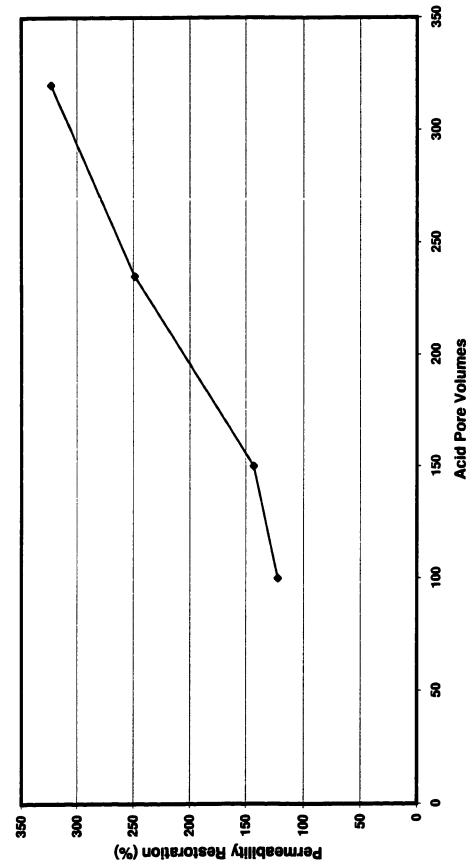
Figure 5.14 Results of permeability restoration Vs acid pore volumes for phase-2
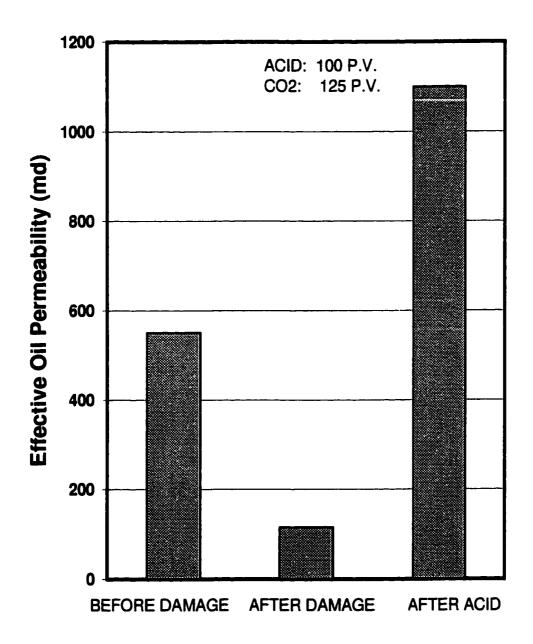
Figure 5.15 Permeability measurement for core M-38

Figure 5.16 Permeability measurement for core M-40

Figure 5.17 Permeability measurement for core M-37
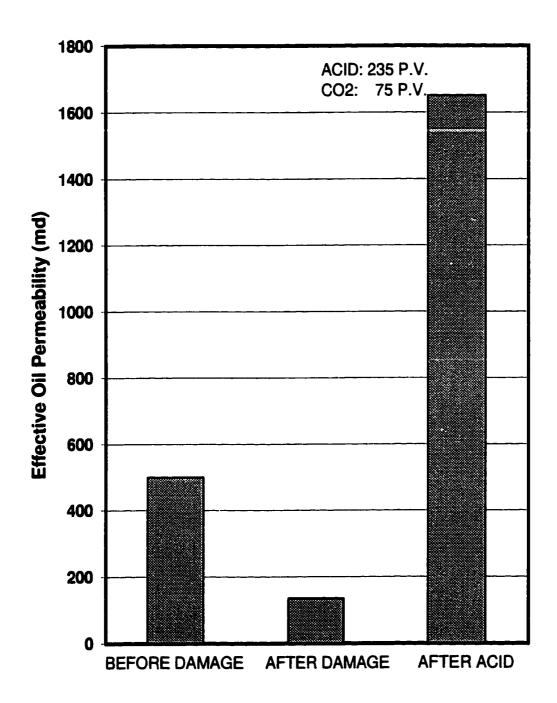
Figure 5.18 Permeability measurement for core M-39

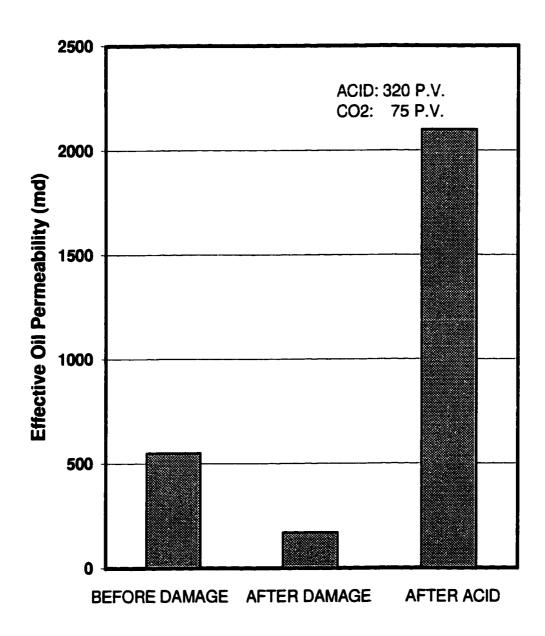Figure 5.19 Permeability measrement for core M-36

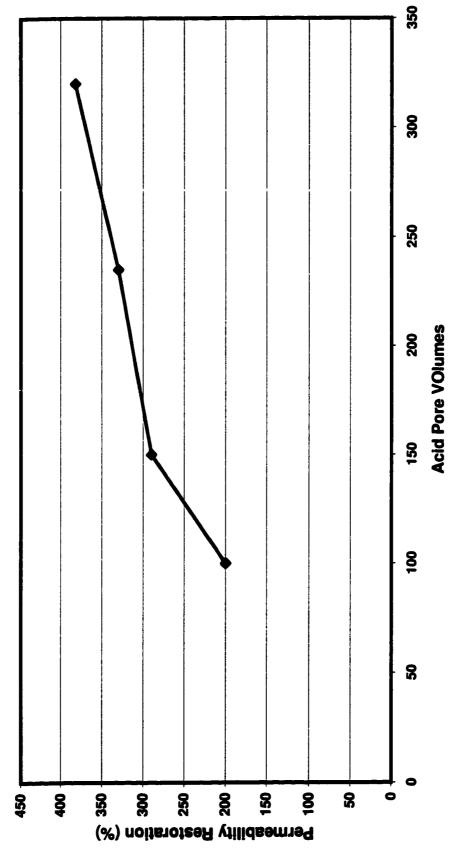Figure 5.20 Permeability measurement for core M-35

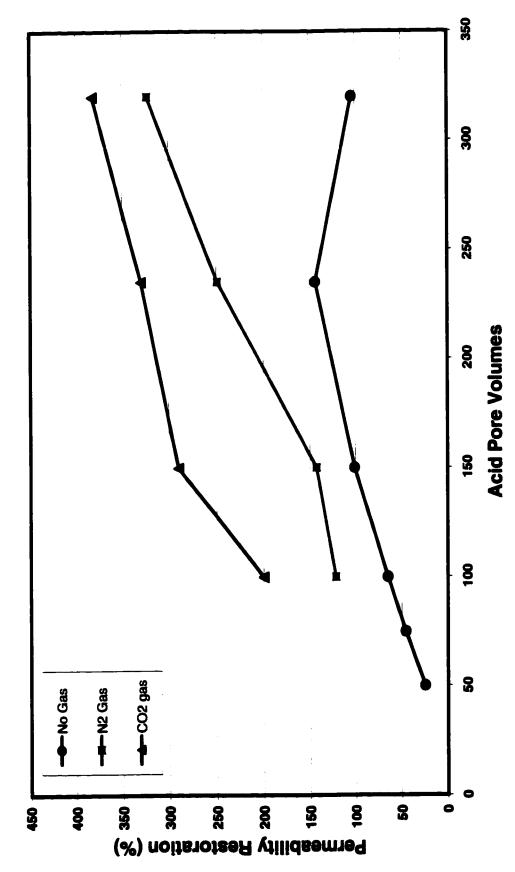Figure 5.21 Results of permeability restoration Vs acid pore volumes for phase-3

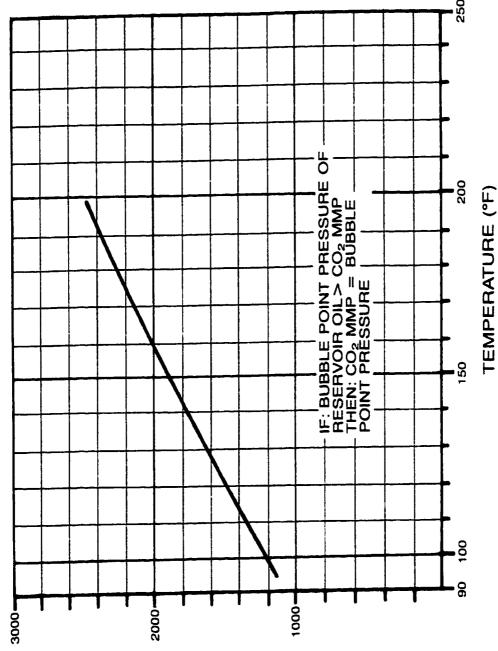Figure 5.22 Results of permeability restoration Vs acid pore volumes for all phases

IF: BUBBLE POINT PRESSURE OF
RESERVOIR OIL > CO₂ MMP
THEN: CO₂ MMP = BUBBLE
POINT PRESSURE

Fig. 5.23 - Temperature/ bubble-point pressure of CO2 MMP correlation (yelling and Metcalfe)
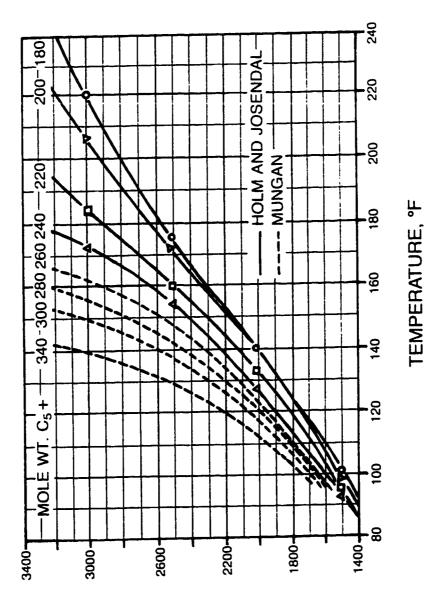
Fig. 5.24 – Pressure required for miscible displacement in CO2 flooding (Holm and Josendal)

Chapter - 6

CHAPTER 6

Summary and Conclusions

1. Laboratory experiments have been conducted to investigate the effect of gas preconditioning prior to acid injection on sandstone matrix stimulation for oil wells.

2. The experiments were performed on Berea core plugs at typical reservoir conditions of 3,000 psi and 180° F. Experiments were conducted in three different phases.

   - Phase-1 was used as basis for research where no preconditioning gas was used.

   - Phase-2 was involved with N_2 gas as preconditioning gas.

   - Phase-3 was involved with CO_2 preconditioning gas.

3. It was found that when acidizing sandstone core plugs with different mud acid volumes without gas preconditioning the restoration in permeability peaked at 235 pore volumes of acid and then decreased.

4. Preconditioning the formation with a gas such as N_2 or CO_2 to displace oil in the zone to be acidized probably improves the relative permeability to aqueous acidizing fluids and increases their effectiveness in stimulating the oil zone.

5. By preconditioning the formation with a gas, the response from acid treatment is roughly proportional to the acid volumes. 100-320 pore volumes of acid were tested.

6. 50-200 gas pore volumes were tested to identify the optimum gas volume. It was found that 75 pore volumes of preconditioning gas provide the minimum gas volume required

7. CO_2 gas is more efficient than N_2 gas because the miscibility pressure for CO_2 is significantly lower than the pressure for the nitrogen gas.

From the results of the present investigation the following recommendations are made for extension to the present work.

1. Larger core plugs are recommended to be used because it can give better representation of stimulation process.

2. Perform one experiment at 5,000 psi reservoir pressure for both N2 and CO2 gas to compare the results between the preconditioning gases

3. Use another type of preconditioning gas such as natural gas

4. Use light and heavy type crude oils

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