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Lisa Akdim, Samia Mokrani Zidi

-TOPIC-

Study of retarded agent performance in acid fracturing technique

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Judges:

President :	Mr.LEBTAHI Hamid	MCB	Ouargla University
Examiner :	Ms.BOUFADES Djamila	MCB	Ouargla University
Supervisor :	Mr.ABDELMADJID Dobbi	Professor	Ouargla University
Co-Supervisor :	Mr.GUENAOUI Ali Seyfedine	Doctor	Ouargla University

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Abstract

Acid fracturing is a well stimulation technique mainly applied to carbonate formations. It is employed to bypass existing formation damage or stimulate an undamaged formation in low permeability reservoirs. During the injection of the acid, it reacts immediately with the formation and for this reason using OPR technology to retard the reaction of the acid with the formation to ensure a long penetration of the acid and gives better results and a best recuperation of the hydrocarbons. In this study a comparison between HCl and retarded agent will be studied including laboratory experiments. The results obtained from these experiences prove that the retarded agent retards the rate of reaction of the acid, after one hour the solubility of carbonate in OPR is 45% and the solubility of the carbonate in HCl is 67%.

Keywords: OpenPath Reach, hydrochloric acid (HCl), retarded agent, acid fracturing, wormholes, leak-off, etched fracture.

Résumé

La fracturation acide est une technique de stimulation de puits principalement appliquée aux formations carbonatées. Elle est utilisée pour contourner les endommagements existants dans la formation ou pour stimuler une formation non endommagée, en particulier dans les réservoirs à faible perméabilité. Lors de l'injection de l'acide, celui-ci réagit immédiatement avec la formation. Pour cette raison, l'utilisation de la technologie OPR est employée pour retarder la réaction de l'acide avec la formation, afin d'assurer une pénétration prolongée de l'acide et obtenir de meilleurs résultats et une meilleure récupération des hydrocarbures. Cette étude porte sur une comparaison entre l'HCl et un agent retardant, incluant des expériences en laboratoire. Les résultats obtenus à partir de ces expériences prouvent que l'agent retardateur retarde le taux de réaction de l'acide. Après une heure, la solubilité du carbonate dans l'OPR est de 45% et la solubilité du carbonate dans l'HCl est de 67%.

Mots clés : OpenPath Reach, acide chlorhydrique (HCl), agent retardateur, fracturation acide, Trous de ver, Fuite, Fracture gravée.

تلخيص

التكسير الحمضي هو تقنية تحفيز الآبار تُطبَّق بشكل رئيسي على الصخور الكربوناتية. يتم استخدامها لتجاوز الترسبات الموجود في التكوين أو تحفيز تكوين غير تالف وفي خزانات النفاذية المنخفضة. أثناء حقن الحمض، يتفاعل مع التكوين فوراً، ولهذا السبب يتم استخدام تكنولوجيا OPR لتباطؤ تفاعل الحمض مع التكوين لضمان اختراق طويل للحمض وتحقيق نتائج أفضل واسترداد أفضل للهيدروكربونات. في هذه الدراسة سيتم دراسة مقارنة بين حمض الهيدروكلوريك (HCl) ووكيل متباطئ، بما في ذلك التجارب المخبرية.

النتائج التي تم الحصول عليها من هذه التجارب تثبت أن العامل المؤخر يؤخر معدل تفاعل الحمض. بعد ساعة واحدة، تكون قابلية انحلال الكربونات في ال OPR 45%، وقابلية انحلال الكربونات في حمض الهيدروكلوريك 67%.

الكلمات المفتاحية: الوصول المفتوح الممر، حمض الهيدروكلوريك (HCl)، الوكيل المُبطّأ، تكسير حمضي، ثقوب الديدان، تسرب، تشقق مُنقوش.

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List of abbreviations

OPR	OpenPath Reach.
HCl	Hydrochloric acid.
HF	Hydrofluoric acid.
$CaCl_2$	Calcium chloride.
CO_2	Carbon dioxide.
H_2O	Water.
KGD	Kristianovich- Geerstma Klerk model.
PKN	Perkins- Kern- Nordgren model.
2D	Two dimensional.
P-3D	Pseudo three dimensional.
PL-3D	Planar three dimensional.
$CaCO_3$	Calcium carbonate
VDA	Viscoelastic diverting acid**.**
NaOH	Sodium Hydroxide.
BHP	Bottom hole pressure.
BHT	Bottom hole temperature.
T	Temperature.
CT	Coiled Tubing.
SDA	Self-Diverting Acid.
LCA	Leak off Control Acid
$CaMg(CO_3)_2$	Dolomite, calcined. Calcium magnesium carbonate oxide.
$MgCl_2$	Magnesium chloride.
HCOOH	Formic acid.
CH_3COOH	Acetic acid.
slb	Schlumberger.

Nomenclature

S	Skin.
bbl	Barrel.
J	Productivity index.
k	Permeability.
q	Oil rate in bottom hole conditions.
h	Reservoir height.
µ	Oil viscosity.
DegC	Degree Celsius, temperature
degF	Degree Fahrenheit, Temperature.
Xf	Fracture half-length.
ft	Feet.

General Introduction

Reservoirs are rocks that have the ability to store fluids inside their pores, so that the fluids (water, oil, and gas) can be accumulated. Reservoirs can be naturally low permeable or they can be damaged by reducing the original or natural permeability of the reservoir rock near the well bore due to several factors during the production period.**[1]**

Well stimulation technique is recommended to increase production by improving the flow of hydrocarbons from the reservoir into the well bore by restoring flow capacity which is performed below fracture pressure, its procedures are wellbore clean-up and matrix treatment or by create new flow capacity which performed above fracture pressure, its procedure is hydraulic fracturing (acid or propped).

Fracturing increases well productivity by creating a highly conductive path into the reservoir that is connected to the wellbore by creating propped fracture using proppant in sandstone reservoirs or creating etched fracture by using acid in carbonate formations.

Acid fracturing has been the preferred alternative stimulation method in carbonate formations in which acid is used for creating a fracture. The acid used is HCl but it has insufficient results. This circumstance can be explained by unachieved planed fracture geometry parameters and low retained fracture conductivity due to the fast reaction of HCl with the carbonate and doesn’t penetrate to the desired distance. HCl is combined with retarded agent (OpenPath Reach) to ensure a long penetration of the acid and to give better results during the acid fracturing operation. OpenPath Reach is a retarded acid with high dissolution capacity, it reduces reaction rate and allows to penetrate more deeply into the fracture.

The goal of acid fracturing is to create sufficient fracture length and restores well productivity by using retarded agent which allows to the acid to penetrate more deeply into the fracture reducing the rate of reaction between the acid and the carbonate.

The acid fracturing technique with OPR technology is used by many countries before Algeria like Tunisia (in 2016), UAE (in 2017) and Qatar (in 2019).

The objective of the present project is to study of retarded agent performance in acid fracturing technique**.** The problematic that will arise from this objective is:

‘What is the retarded agent performance in acid fracturing technique?’

In order to highlight this technique and respond to the problematic raised, the follow plan is followed. This work has been divided into following chapters:

The first chapter “Reservoir damage & well stimulation” includes a view of formation damage and the different types and mechanisms of damage, followed by a discussion of the methods used to identify and quantify this damage in oil and gas wells.

Well stimulation technique is the most effective method to occur the problem of damages by going to hydraulic fracturing.

The second chapter “Acid fracturing technique” aims to give an introduction to acid fracturing technique. It focuses on the concept, advantages, mechanics, the selection of candidate wells and fluids had chosen of this operation are also discussed.

In the third chapter “Comparison study of OPR & HCl” includes an experimental study to study the performance of retarded agent on acid frac technique and to compare HCl acid with OPR.

It includes also a case of study of a field to show the performance of OPR.

Chapter I:

Reservoir Damage & Well Stimulation

Chapter I: Reservoir damage & well stimulation

I.1 Introduction

Reservoirs are rocks that have the ability to store fluids inside their pores, so that the fluids can be accumulated.

Reservoir rocks that contain petroleum must be both porous and permeable so for that reason reservoir rocks are dominantly sedimentary (sandstones and carbonates). **[2]**

The reservoirs can be classified as conventional or unconventional based on the technological requirements for development and production.**[3]**

Reservoirs can be naturally low permeable or they can be damaged due to several factors during the production period. **[4]**

For removing the difficult damages and create a new permeability in low permeability reservoirs the technique of well stimulation is recommended by using matrix acidizing or hydraulic fracturing.

I.2 Damage concept

Formation damage can be defined as the reduction of the original or natural permeability of the reservoir rock near the well bore. It can also be defined as any type of a process which leads to a reduction of the productivity of oil and gas productivity in many reservoirs.**[5]**

Formation damage is an undesirable operational and economic problem that can occur during the various phases of oil and gas recovery from subsurface reservoirs including production, drilling, hydraulic fracturing, and work over operations**.** **[5]**

Formation damage indicators include:

- Permeability impairment.
- Skin damage.
- Decrease in well performance. **[5]**

I.2.1 Mechanismes of formation damage

Evaluating formation damage appears daunting with the large number of mechanisms present. Technology exists in numerous situations to allow an accurate determination of the types of damage to which a given reservoir is susceptible.

There are four primary mechanisms of formation damage:

1) Mechanical.
2) Chemical.
3) Biological.
4) Thermal. **[6]**

I.2.2 Mechanical mechanisms

Mechanical damage mechanisms are related to a direct, non-chemical interaction between the equipment or fluids used to drill, complete, kill, or stimulate a well and the formation resulting in a reduction in the permeability of the formation. Common mechanical impairment mechanisms would include:

- **Fines migrations**

This refers to the motion of naturally existing particulates in the pore system caused by high fluid shear rates. These may include various types of uncemented clays.**[6]**

- **External solids entrainment**

This refers to the invasion of particulate matter suspended in drilling or other fluids which may be injected or exposed in an overbalanced condition to the rock matrix surrounding the wellbore. **[6]**

- **Phase trapping and blocking**

This is related to a combination of adverse capillary pressure and relative permeability effects. The basis of a phase trap is a transient or permanent increase in trapped fluid saturation in the pore system surrounding the wellbore, causing a reduction in relative permeability to the phase which it’s desired to produce or inject.**[6]**

- **Glazing/Mashing**

This refers to direct damage to the wellbore face caused by bit/heat interactions or poorly centralized rotating and sliding pipe in a poor hole cleaning situation, resulting in the working of fines and cuttings into the formation face. **[6]**

- **Perforation damage**

The detonation of perforation charges may result in the creation of a crushed zone and generate mobile fines adjacent to the perforation tunnel, possibly reducing the permeability in this region.

The composition of the perforating fluid, if perforating overbalanced, may also have a significant impact on damage effects. **[6]**

- **Proppant crushing and embedment**

This is a damage mechanism which can reduce the effective conductivity of an artificially generated hydraulic fracture. Normally a proppant (sand) is placed to hold the fracture open after the fracture pressure has been released to maintain high permeability to the newly accessed portion of the reservoir. **[6]**

I.2.3 Chemical damage

Chemical damage mechanisms include:

- **Clay swelling**

This is another mechanism of formation damage and involves the interaction and hydration of hydrophilic materials, such as smectite or mixed layer clays, by reaction with fresh or low salinity water. **[6]**

- **Clay deflocculation**

Less understood but often more common in occurrence than clay swelling, clay deflocculation is caused by a disruption of the electrostatic forces holding the surfaces of individual clay units. **[6]**

- **Chemical adsorption**

Polymers and other high molecular weight materials present in some fluids may become bound or adsorbed on the surface of the formation matrix and clays and, by virtue of their large molecular size, cause restrictions in flow area and hence permeability. **[6]**

- **Formation dissolution**

Certain formation components (halite, various shales, anhydrite, etc.) may have limited to high solubility in water-based fluid. **[6]**

- **Paraffins and Waxes**

Many oils exhibit low temperatures which can result in the precipitation of crystalline in non-alkane based solid hydrocarbons, or “waxes,” from solution in the oil. **[6]**

- **Emulsions**

Emulsions often occur in oilfield operations. The most common type of problematic emulsion is the “water internal emulsion” in which small droplets of water are encapsulated in a continuous external oil phase. **[6]**

- **Wettability alterations**

Many additives to oilfield fluids, particularly many surfactants, defoamers, corrosion inhibitors, and some biocides, have polar adsorptive tendencies which may cause them to establish an oil wetting condition in the region of the reservoir in which they invade. **[6]**

- **Other solids**

A wide range of organic and inorganic solids may also precipitate from reservoir fluids and result in plugging difficulties downhole, in tubing, or surface or injection equipment. **[6]**

I.2.4 Biological damage

This type of damage refers to problems created by the introduction of viable bacteria and nutrient streams into a reservoir. Although most commonly associated with water injection operations, bacterial contamination has the potential to occur any time a water-based fluid is introduced into a formation. **[6]**

I.2.5 Thermal damage

Thermal damage mechanisms refer to those associated with high temperature injection operations (steam injection,… etc.). These include:

- Mineral transformation.
- Wettability alternation.
- Thermal degradation.
- Reduction in absolute permeability.
- Dissolution. **[6]**

I.2.6 Damage location

- **Surface:** Flow lines, valves…
- **Wellbore:** Tubing, casing/liner, accessories (nipples, SSSV, ESP…)
- **Completion:** Perforation, gravel pack, screen…
- **Formation:** Formation damage specifically refers to obstructions in the near-wellbore region of the reservoir. **[7]**

I.2.7 Quantifying formation damage

A commonly used measure of well productivity is the productivity index J (bbl/psi).**[8]**

$$J = \frac{q_0}{P_R - P_{WF}} \qquad (I.1)$$

The most commonly used measure of formation damage in a well is the skin factor (S). The skin factor is a dimensionless pressure drop caused by a flow restriction in the near-wellbore region. It is defined as follows:

$$S = \left(\frac{kh}{141.2\ q\mu B}\right)\Delta P_{skin} \qquad (I.2)$$

k: permeability.
h: Reservoir height.
q: Oil rate in bottom hole conditions.
µ: Oil viscosity.
B: Volumetric factor.

Figure (I.1) below shows how flow restrictions in the near-wellbore region increase the pressure gradient, resulting in an additional pressure drop caused by formation damage (ΔPskin).**[8]**

$$F = \frac{P_R - P_{WF} - \Delta P_{skin}}{P_R - P_{WF}} = \frac{\text{actual drawdown}}{\text{ideal drawdown}} \qquad (I.3)$$

P_R: Reservoir pressure
P_{WF}: flowing bottomhole pressure

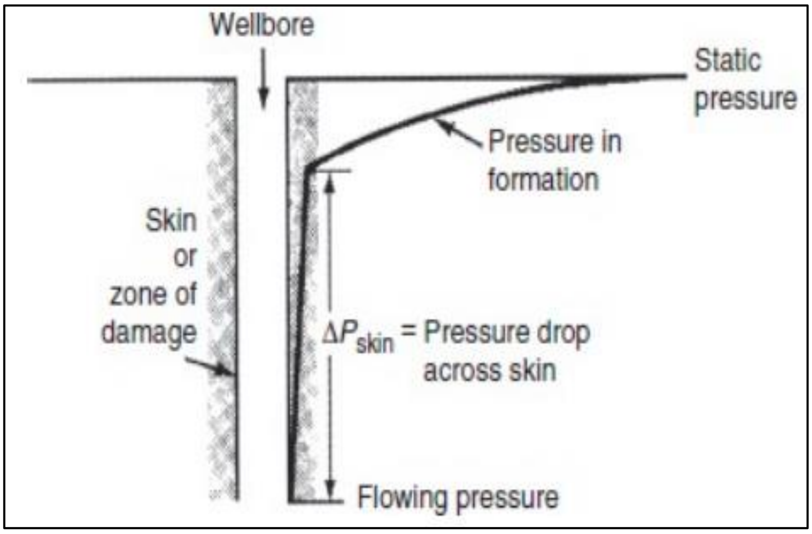

Figure I.1: Pressure profile in the new well-bore region for a well with formation damage.**[8]**

A flow efficiency of 1 indicates an undamaged well with $\Delta P_{skin} = 0$. Flow efficiency greater than unity indicates a stimulated well (perhaps because of a hydraulic fracture) **S>1** and a flow efficiency < **1** indicates a damaged well. Note that to determine the flow efficiency, we must know the average reservoir pressure and the skin factor introduction to Hydraulic Fracturing.

I.3 Well stimulation concept

Well stimulation is a well intervention performed on an oil or gas well to increase production by improving the flow of hydrocarbons from the reservoir into the well bore.**[9]**

I.3.1 Stimulation technique

- **Restores Flow Capacity:** is a technique which is performed below fracture pressure. Its procedures are wellbore clean-up and matrix treatment.**[10]**
- **Create New Flow Capacity:** is a technique which performed above fracture pressure. The procedure is hydraulic fracturing (acid or propped).**[10]**

I.3.2 Definition of hydraulic fracturing

Fracturing is a stimulation technique performed above-formation fracturing pressure. Fluid is pumped at a pressure above the fracture pressure of the reservoir to create fractures within the rock itself. It increases well productivity by creating a highly conductive path into the reservoir that is connected to the wellbore.

I.3.3 Hydraulic fracturing objectives

In general, hydraulic fracture treatments are used to increase the productivity index of a producing well or the injectivity index of an injection well. The productivity index defines the volumes of oil or gas that can be produced at a given pressure differential between the reservoir and the wellbore.**[11]**

There are many different objectives of hydraulic fracturing depending upon certain situations. For instance, hydraulic fracturing is used to:

1. Increase the flow rate of oil and/or gas from low permeability reservoirs.
2. Increase the flow rate of oil and/or gas from wells that have been damaged.
3. Connect the natural fractures in a formation to the wellbore.
4. Decrease the pressure drop around the wellbore.
5. Increase the area of drainage or the amount of formation in contact with the wellbore.
6. Connect the full vertical extent of the formation to the wellbore.**[11]**

I.3.4 Hydraulic fracturing fundamentals

I.3.4.1 Candidate selection

The success or failure of a hydraulic fracture treatment often depends on the quality of the candidate well selected for the treatment. The most critical parameters for hydraulic fracturing are:

- Formation permeability.
- The in-situ stress distribution.
- Reservoir fluid viscosity.
- Skin factor.
- Reservoir pressure.
- Reservoir depth.
- The condition of the wellbore.**[11]**

I.3.4.2 Propped and acid fracturing

- **Propped fracturing**

When pumping stops and the fluid leaks off, the pressure from the surrounding rock forces the fracture to close. To keep the fracture open, a propping agent is added to the fluid. When the pumping stops and fluid leaks off, the proppant remains in the fracture. The fracture is held open by the proppant, creating a permeable and easy path for the hydrocarbons to flow.**[12]**

- **Acid fracturing**

Acid fracturing, also called fracture acidizing, is a stimulation process in which acid is injected into a formation at a pressure that is sufficient to fracture the formation. Acid fracturing treatments are pumped in carbonate formations that are highly soluble in the acid system being pumped. The acid etches the face of created hydraulic fracture, so that when the fracture tries to close following the treatment the unevenness of the etching pattern on the fracture-face results in a conductive pathway for hydrocarbons to flow to the wellbore. **[12]**

Figure (I.2) represents propped and etched fracture.

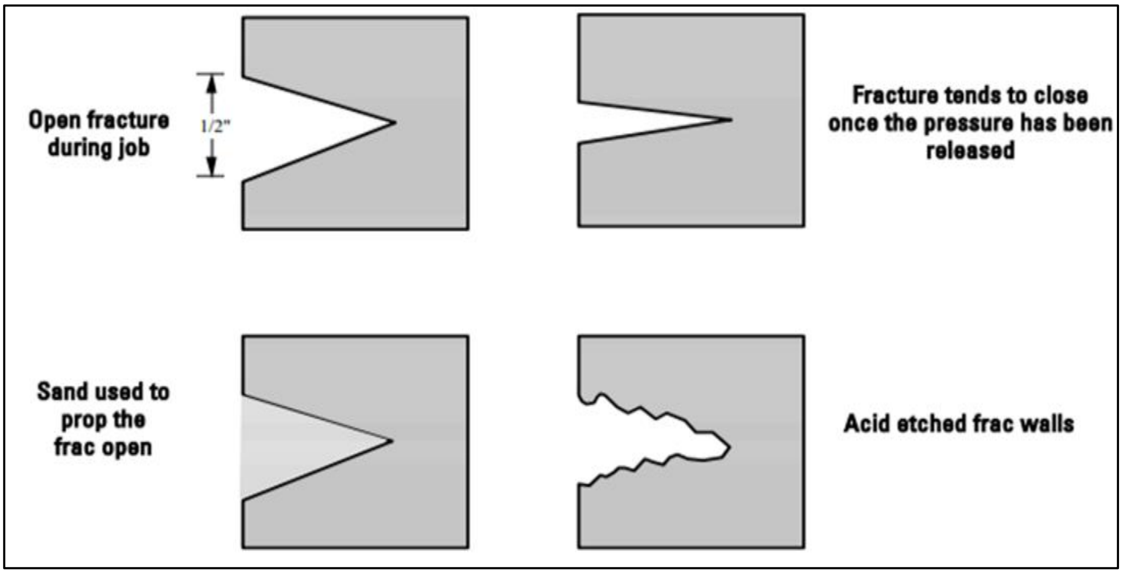

Figure I.2 : Propped & Etched fracture. **[15]**

I.3.4.3 Fracturing fluid

The fracturing fluid is a critical component of the hydraulic fracturing treatment. Its main functions are to initiate and propagate the fracture and to transport propping agent along the length of the fracture.

I.3.4.4 Fluid types

- **Water-based fluids**

Water-based fluids are the most common fluids used in fracturing because of their lower cost, high performance, and ease of handling.**[12]**

- **Oil-based fluids**

Hydrocarbons were used originally as fracturing fluids because they were perceived as less damaging to the formation than water-based fluids. Oil-based fluids are expensive to use and operationally difficult to handle along with the increased safety risk. **[12]**

- **Acid-based fluids**

The acid-based fluid is usually used to fracture carbonate formations in what is called acid fracturing technique. It presents higher operational risk. **[12]**

- **Multiphase fluids**

- **Foams:** Foams are another way to enhance the properties of fracturing fluid. Adding gas to a fluid creates foam a stable mixture of liquid and gas.

- **Emulsions:** An emulsion is a dispersion of two immiscible phases, such as oil in water or water in oil stabilized with surfactant. Emulsion-based fracturing fluids are highly viscous solutions with good proppant transport properties and are used very infrequently today. **[12]**

I.3.4.5 Fracturing fluid components

Fracturing fluid can have several components added to it to adjust its properties:

- **Gelling Agents:** Gelling agents are used to thicken the fluid. Common gelling agent is Guar. **[15]**
- **Additives:** Various additives have been developed to enhance the performance of fracturing fluids (Table I.1). **[12]**

Table I.1 : Fracturing fluids additive. **[12]**

Additives	Description
Crosslinkers	Crosslinking agents are used to increase the molecular weight of the polymer, therefore increasing the viscosity of the solution.
Buffers	The stability and crosslinking rate performance of some crosslinked gels is affected by the pH of the fluid. Buffers are weak acids or bases that are added to the fracturing fluid to control the pH balance.
Clay Stabilizers	Clay particles can migrate or swell, blocking pore spaces in the rock and reducing permeability. Clay stabilizers are added to water-based fracturing fluids to help prevent formation damage caused by clay.
Bactericides	Enzymes from bacteria can feed on the polymers, degrading a gel’s viscosity.
Temperature Stabilizers	Temperature stabilizers are used to prevent degradation of gels at temperatures greater than 200 degF [93 degC].
Fluid loss additive	Only the fluid that remains in the fracture can propagate cracks in the formation. Fluid that leaks off into the rock formation is wasted,therefore, good fluid-loss control is essential for an efficient fracturing treatment.

I.3.4.6 Operation stages

- **Pre-pad:** cool the tubulars, cool the formation, break-down formation.
- **Pad:** generate the fracture, control fluid loss.
- **Slurry:** transport/place proppant.
- **Flush:** displace slurry in the tubulars.**[13]**

I.3.4.7 Proppant

Proppants are added to fracturing fluids during the slurry stage. Whatever proppant material is chosen, its function is to hold the fracture open and maintain a permeable path through the hydraulic fracture. Several different types of proppants as it mentioned in figure(I-3) can be used are:

- **Sand:** Sand is the most commonly used proppant. **[12]**
- **Resin-Coated Sand:** A resin coating strengthens the grains of sand and helps bind them together when they are in place to keep them from flowing back toward the well. **[12]**
- **Intermediate-Strength Proppants:** Intermediate-strength, ceramic proppants are manufactured by specialty suppliers. **[12]**
- **High-Strength Proppants:** High-strength proppants are more expensive than intermediate-strength, ceramic proppants and are only used in wells with very high closure pressures. **[12]**

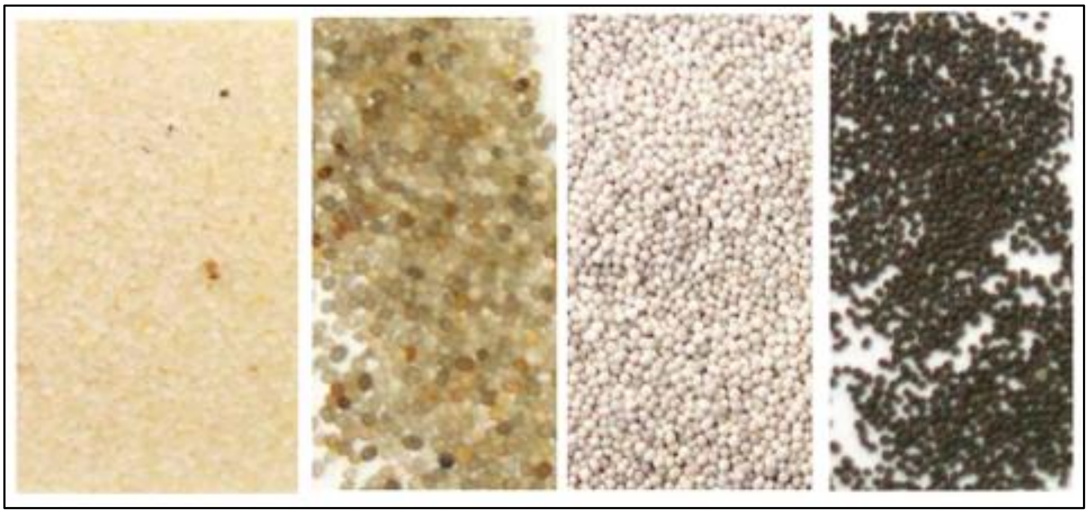

Figure I.3: Different type of proppant.**[14]**

I.3.4.8 Hydraulic fracturing equipment

Hydraulic fracturing equipment are necessary for the success of the operation. Equipments are designed for high-horsepower applications while delivering fracturing fluids to the well at high pressure and high rate in numerous applications, including well stimulation processes (fracturing, acidizing). The different equipment as shown in figure (I.4) are:

- Proppant blender.
- Hydration unit.
- High Pressure Stimulation Pump.
- Sand Chief.
- Manifold Trailer.
- Frac Tank.
- Monitoring unit.
- Batch Mixer.
- Tree Saver.

Figure I.4: Hydraulic fracturing equipment.**[10]**

I.3.4.9 Hydraulic fracturing design

1. **Treatment design objective**

Place an optimum fracture to maximize incremental production. The key to successful fracture stimulation:

- Fracture containment.
- Adequate propped or etched fracture length.
- Adequate fracture conductivity.**[14]**

2. **Data collection**

- **Reservoir Information**
  - Data Requirement.
  - Reservoir evaluation.
  - In situ Stresses.
  - Permeability, Porosity, Temperature.
  - Reservoir pressure.**[14]**
- **Well information**
  - Hole Survey.
  - Completions.
  - Perforations.
  - Well Production history.
  - Well Test.

3. **Rock mechanical proprieties**

Rock mechanics considerations required to model the hydraulic fracture process: Young Modulus, Poisson’s Ratio, In-situ stresses.**[15]**

- **Young Modulus**

It provides relationship between stress-strain. **[15]**

Figure (I.5) shows a graph of stress and deformation (Young Modulus).

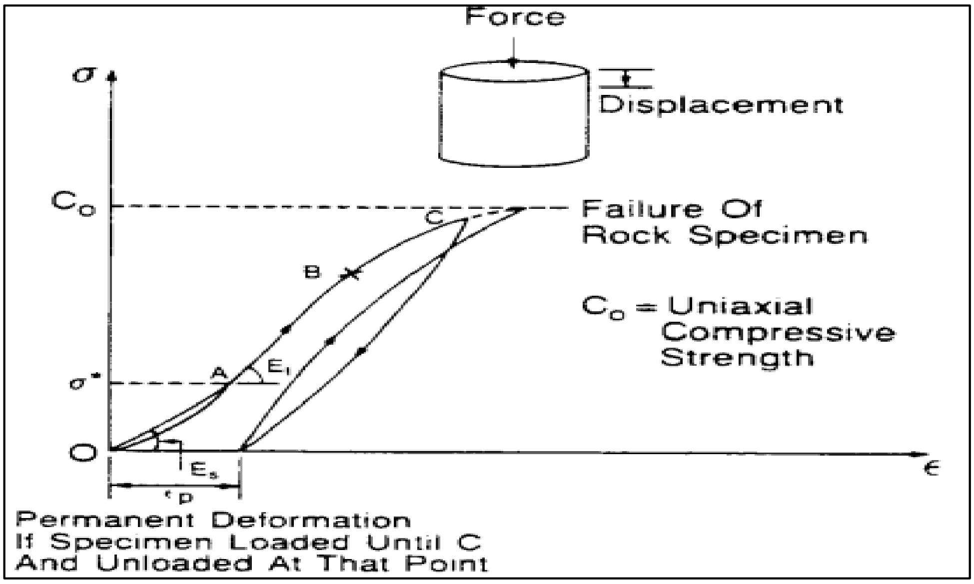

Figure I.5: Graph of stress and deformation (Young Modulus).**[15]**

- **Poisson's ration**

Poisson's ratio is the ratio of transverse contraction strain to longitudinal extension strain in the direction of the stretching force (Figure I.6).**[16]**

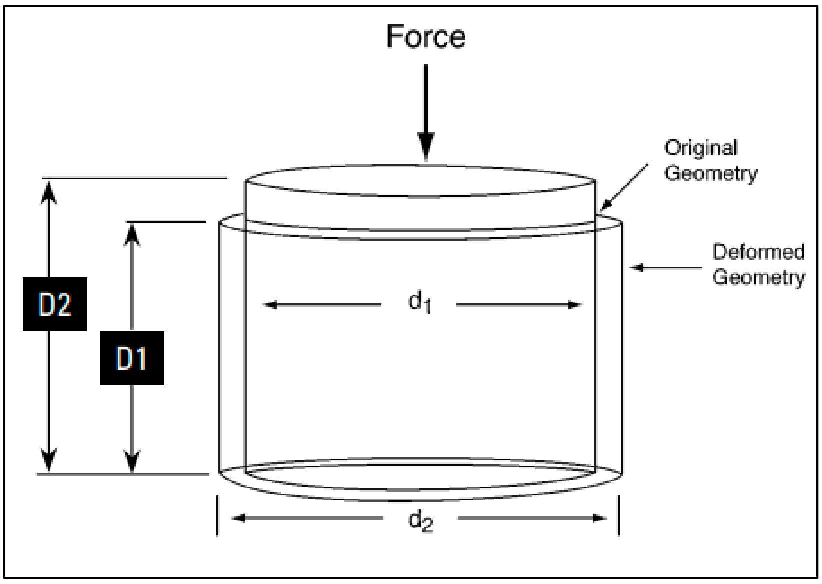

Figure I.6 : Poisson's ratio formula. **[15]**

- **In-situ stresses:**

In Situ Stress is the single most important factor controlling hydraulic fracturing. There are three types of stress as illustrated in figure (I.7):

- **In-Situ Stress:** The collective forces activating on the rock while the rock is in place below the earth's surface.
- **Overburden Stress:** Stress parallel to wellbore axis due to overburden load.
- **Horizontal Stress:** Perpendicular to the overburden stress at the right angles of each.**[15]**

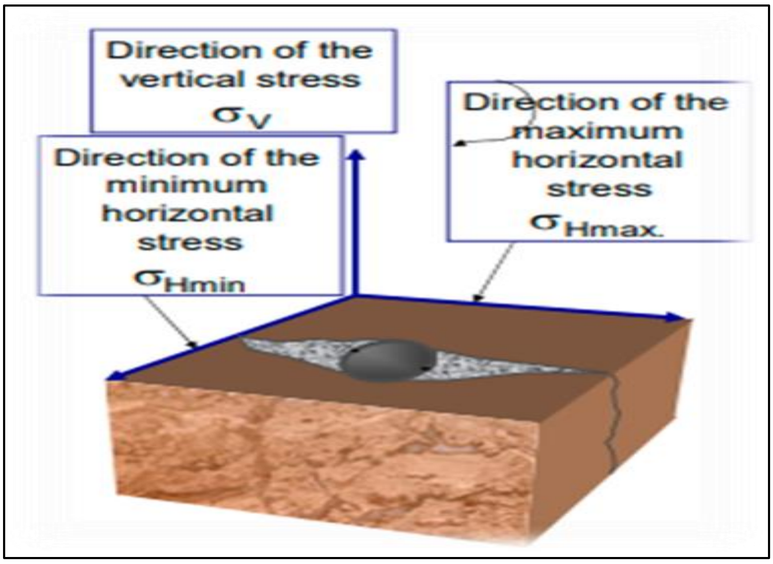

Figure I.7 : Principal compressive stress. **[17]**

4. Fracture modeling:

Prediction of fracture geometry is central issue in engineering design and evaluation. Models determine fracture geometry by relating to variables:

- Rock properties.
- Fluid properties.
- Fluid volume pumped.
- Stress data. **[18]**

Many models have developed currently:

- Two-dimensional (2D).
- Pseudo three-dimensional (P-3D).
- Planar three-dimensional (PL-3D).**[18]**

➢ 2D fracture propagation model

- **KDG fracture model**

Plane strain is in the horizontal direction (upper and lower layers). Free slippage occurs in these faces. Shorter, wider fractures. Pressure decreases in time (Figure I.8). (XL < h). **[18]**

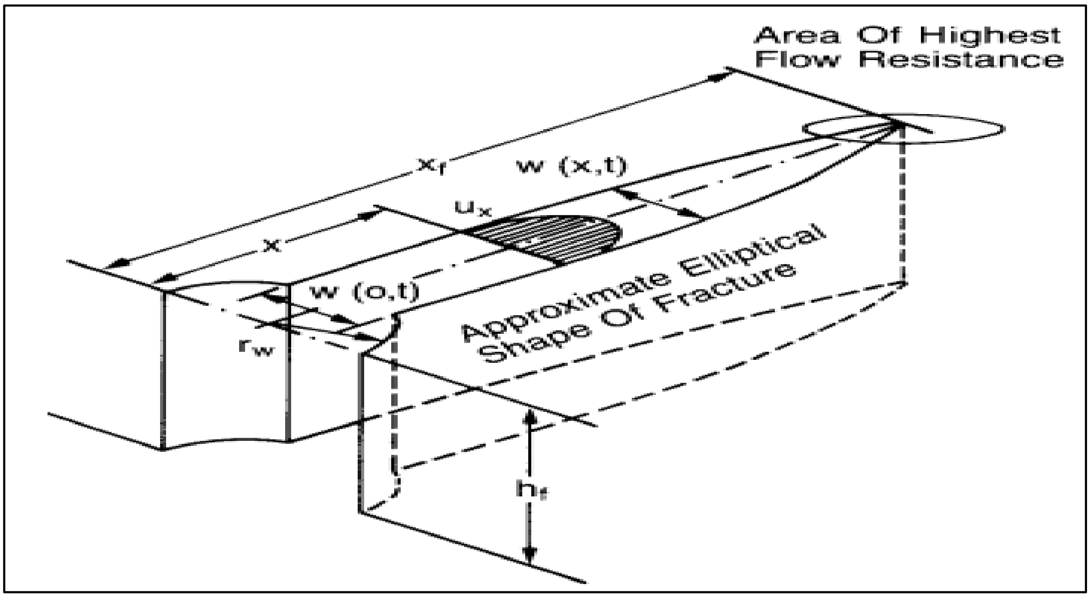

Figure I.8: KGD geometry for a 2D fracture. **[18]**

- **PKN fracture model**

The plane strain is in the vertical direction (occurs on the front and back layers). Free slippage occurs in these faces (Figure I.9). Longer, narrower fractures. Pressure increases in time. (XL > h). **[18]**

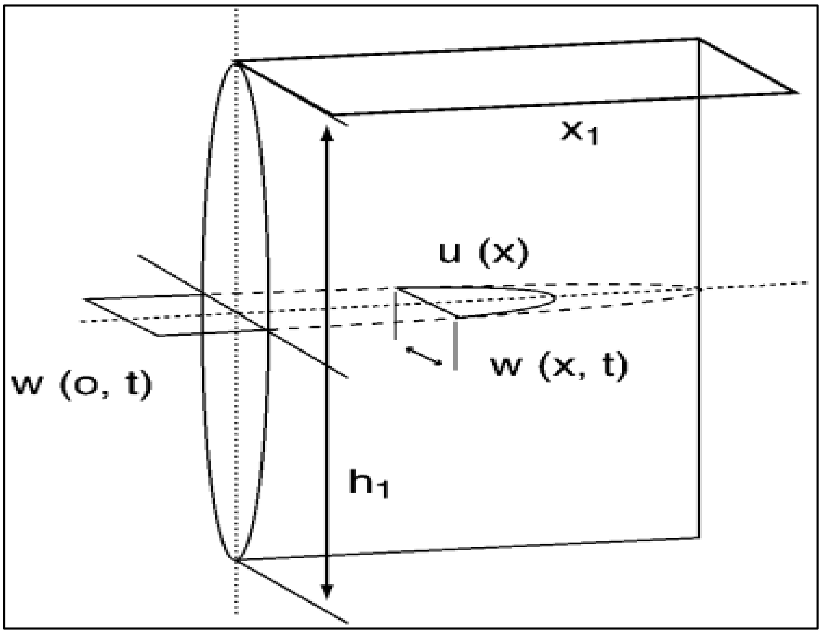

Figure I.9: PKN geometry for a 2D fracture.**[18]**

- **Radial fracture model**
  - Similar to the KGD model.
  - Vertical radial: Massive, homogeneous formations (Figure I.10).
  - Horizontal radial:

- shallow depths.
- highly geopressured formations. **[18]**

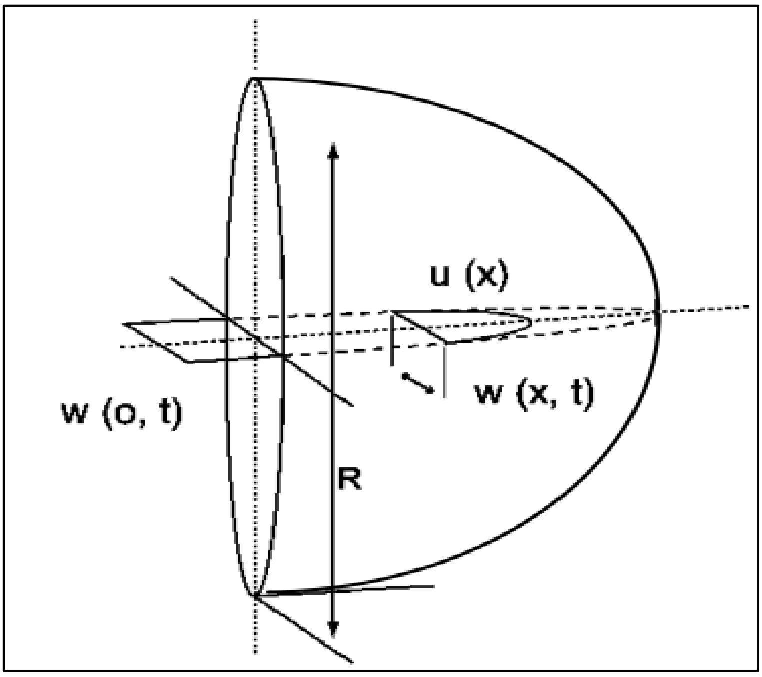

Figure I.10: Radial Model geometry for a 2D fracture.**[18]**

➢ Pseudo three-dimensional (P-3D)

- Pseudo three-dimensional model is the same as the PKN model, that is vertical planes deform independently (Figure I.11).
- The height of the fracture depends on the position along the fracture and the time.
- A vertical fracture will grow in a layered medium as a function of the layer properties.**[18]**

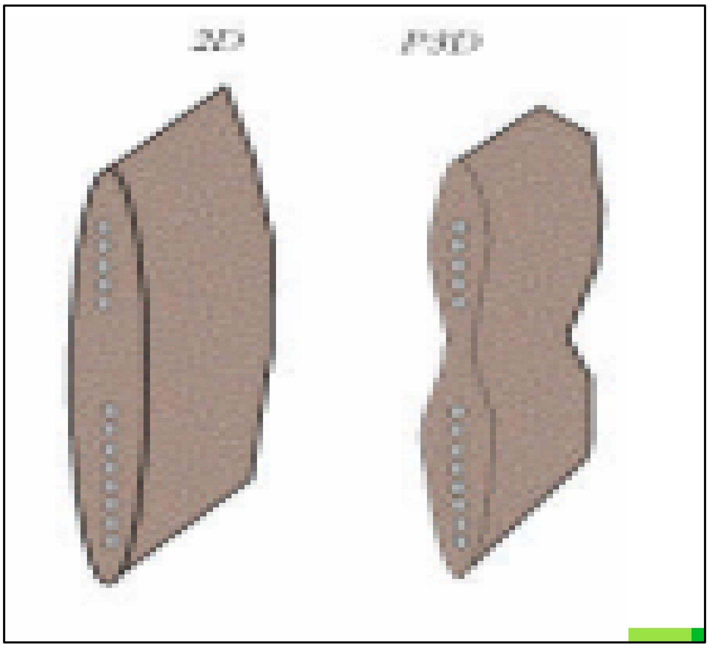

Figure I.11: 2D&P3D fracture geometry.**[17]**

PL 3D models

- Grids in vertical and horizontal direction as it represented in figure (I.12).
- Rigorous proppant and fluid flow calculations.
- 2-D zone stress variation.
- Significantly increased execution time. **[18]**

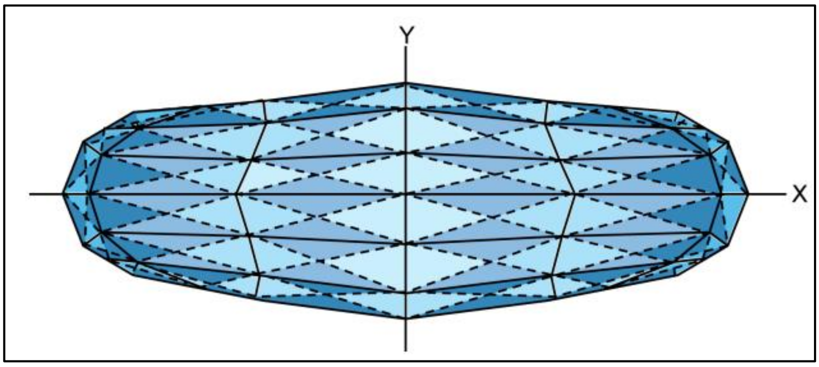

Figure I.12: PL 3D fracture geometry.**[18]**

I.4 Conclusion

Hydraulic fracturing is essential for the stimulation of the reservoirs which are damaged or they have a low permeability. The fracturing technique is used in both sandstone by using the proppant and carbonate reservoirs by using acid.

Chapter II:

Acid Fracturing Technique

Chapter II: Acid fracturing technique

II.1 Introduction

Acid fracturing has been the preferred alternative stimulation method in carbonate formations. It restores the communication to the fissured system in productive formation often damage by mud losses during drilling. Acid fracturing treatment of the formation is to achieve productivity or injectivity beyond the natural capabilities of the reservoir. It is most applicable in formations with a low and/or ineffective permeability structure.**[19]**

II.2 Acid fracturing definition

Acid fracturing is a common well stimulation technique mainly applied to carbonate formations. It is employed to bypass existing formation damage or stimulate an undamaged formation. Acid fracturing is a technique used in the oil and gas industry to increase the production of hydrocarbons from low-permeability reservoirs. It involves injecting a solution of acid and other chemicals into a wellbore at high pressure to create fractures in the surrounding rock formation (FigureII.1).**[20]**

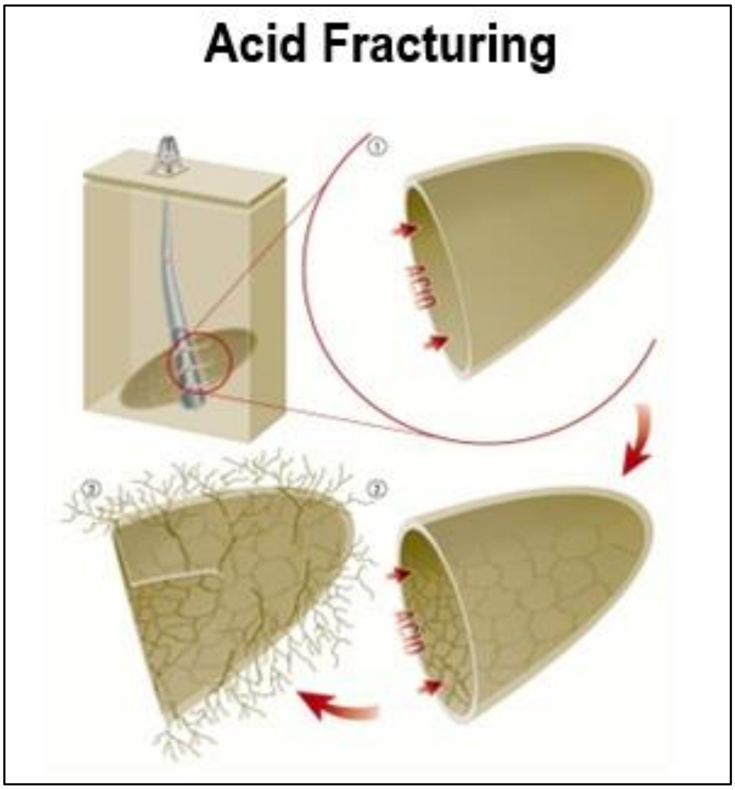

Figure II.1: Acid fracturing.**[21]**

II.3 Acid fracturing objective

The goal is to create sufficient fracture length and restore well productivity.

II.4 Principe of acid fracturing

- Acid is injected above fracturing pressure: a hydraulic fracture is created.
- Possible in both limestone and dolomite.
- Fracture faces are dissolved and etched: conductive channels are created.
- Length of etched fracture determined by acid type, volume, pump rate, leak off parameters, and spending rate.
- Effectiveness determined by fracture length and fracture conductivity.**[22]**

II.5 Candidates for acid fracturing

- Cleaner limestone and Dolomite formations: they must have good fracture containment to generate length.
- Dirty carbonate rocks (< 70% solubility in HCl) are poor candidates because acid etched channel will be impaired and release of insoluble material will plug the channel.
- Chalk formations may not be suitable because they are soft and unable to retain conductivity after closure.
- Not applicable to sandstone formations because HCl or HF will not adequately etch sandstone fracture face and materials released through dissolution will plug the fracture.**[22]**

II.6 Advantages of using the acid fracturing

- The treatments are more conservative in that there is a low risk of failing to complete the treatment.
- They provide infinite conductivity and can strongly enhance natural fracture permeability.
- They are easier to divert in thick-formation intervals using ball sealers or chemical diverters.
- They are simpler to conduct operational especially in very remote locations or off a stimulation boat.
- They are much less expensive than propped fracturing especially offshore.**[23]**

II.7 Acid fracture mechanics

Acid fracturing mechanics are acid leak off, acid reaction and acid transport as they represented in figure (II.2).

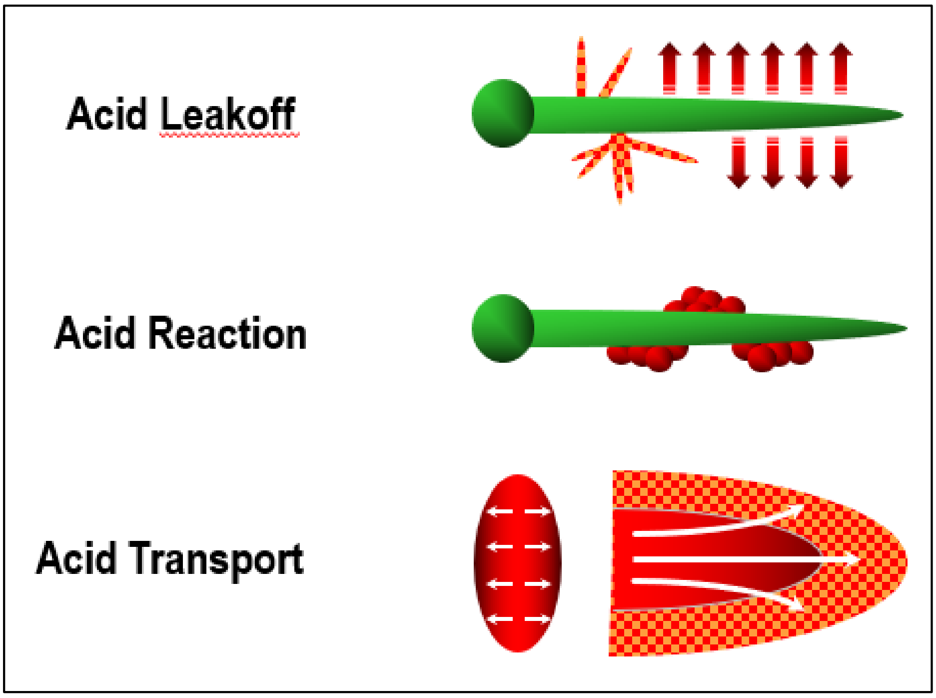

Figure II.2: Acid Fracture Mechanics.**[24]**

II.7.1 Acid leak off

- Acid leak off causes the decline in treating during pumping:
    - Fracture extension becomes restricted.
    - Conventional filter cakes are destroyed by the acid.
- Natural fissures and fractures:
    - Fissures widen as more acid is introduced.
    - Limit the fracture propagation.
- Leak off dictated by:
    - Reservoir fluid mobility & compressibility.
    - Acid viscosity.
    - Wormholes. **[24]**

II.7.1.1 Leak off control

Deferent ways of leak off control are represented in table (II.I).

Table II.I: Leak off control. **[24]**

VDA	LCA/SDA	Control natural fracs
– Viscosity increases as acid spends. – Increases resistance ahead of wormhole tip and reduces leak off rate. –Non-damaging & simple mixing.	– Crosslinking as acid spends. – Potential gel damage. –Complex chemistry/mixing.	– 100-mesh sand. – Fibers. –MaxCO$_3$ (VDA with Fibers).

II.7.1.2 Wormhole development

This is a phenomenon where acid eats a preferential channel into the reservoir, significantly increasing fluid loss. It's the major source of leak off, limiting penetration. Wormholes also reduce fracture width and forms in the porosity of rock matrix. Figure (II.3) represents wormholes. They are affected by temperature, acid concentration and injection rate.**[24]**

Figure II.3: Wormholes.**[24]**

II.7.2 Acid reaction

Defined as the number of molecules reacting with the carbonate rock per unit of time. It is the speed at which the acid reacts. **[24]**

$$\frac{\partial M_{acid}}{\partial t} = -K_r(C_{wall} - C_{eqm})^m \qquad (II.1)$$

M_{acid} = moles of acid at fracture wall.

K_r = Reaction rate constant.

C_{wall} = Acid concentration at fracture wall.

C_{eqm} = Equilibrium acid concentration.

Two mechanisms involved:

1. Physical Transportation of acid molecules (Diffusion).
2. The chemical reaction of acid and rock molecules. **[24]**

II.7.2.1 Acid diffusion rate

Acid diffusion is the natural motion of molecules of any fluid. Depends upon temperature and spontaneous movement from a region of higher to lower concentration.

Diffusion is affected by the products generated by the chemical reaction (Reduce temperature to slow diffusion), if turbulence is suppressed, diffusion is slowed.

Reducing surface-reaction rate by reducing temperature (Cooldown) and inserting a barrier in between using filter cake, hydrocarbon barrier or reservoir oil.**[24]**

Figure (II.4) represents diffusivity in function of temperature.

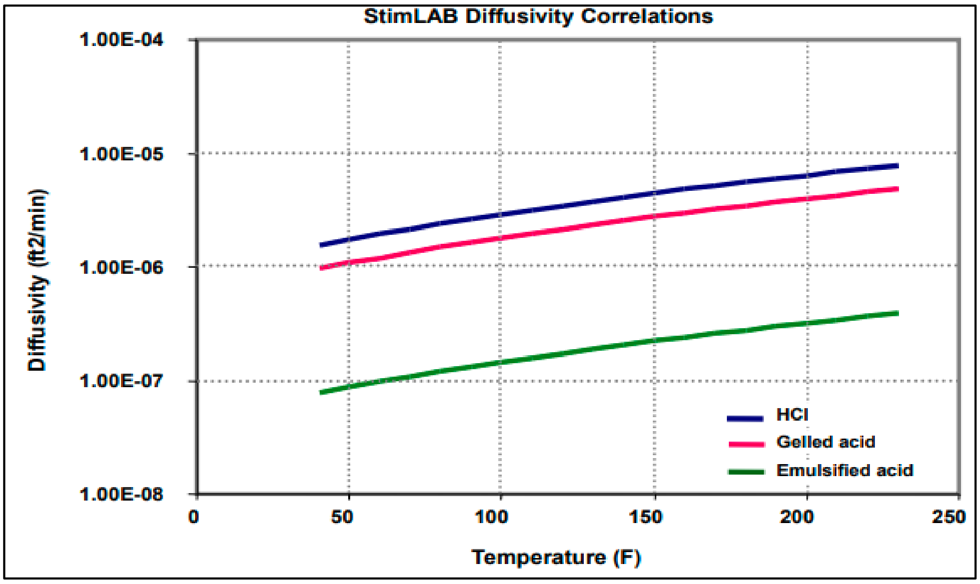

Figure II.4: Graph of diffusivity in function of temperature. **[24]**

II.7.2.2 Acid penetration

Factors affecting etched fracture length are:

1. **Acid leak-off**

Figure (II.5) illustrates acid leak off.

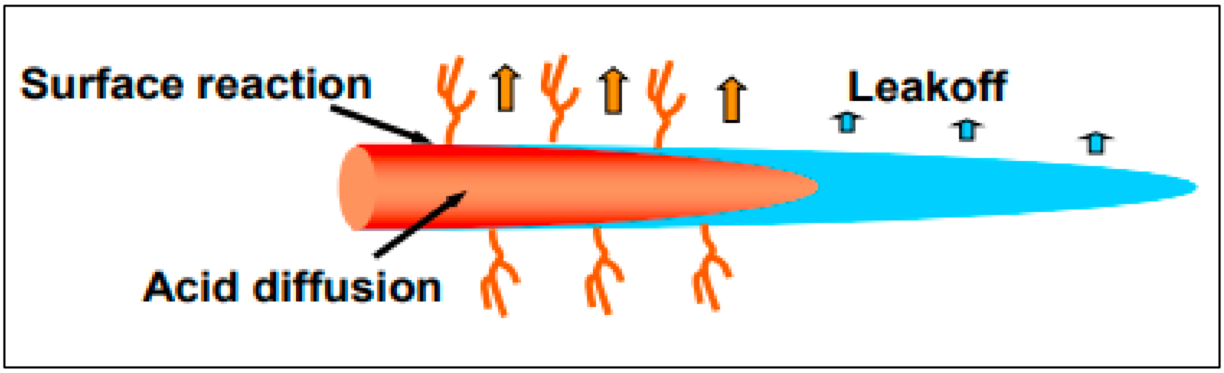

Figure II.5: Acid leak off.**[24]**

2. **Acid spending rate**

The acid spending is shown in figure (II.6).

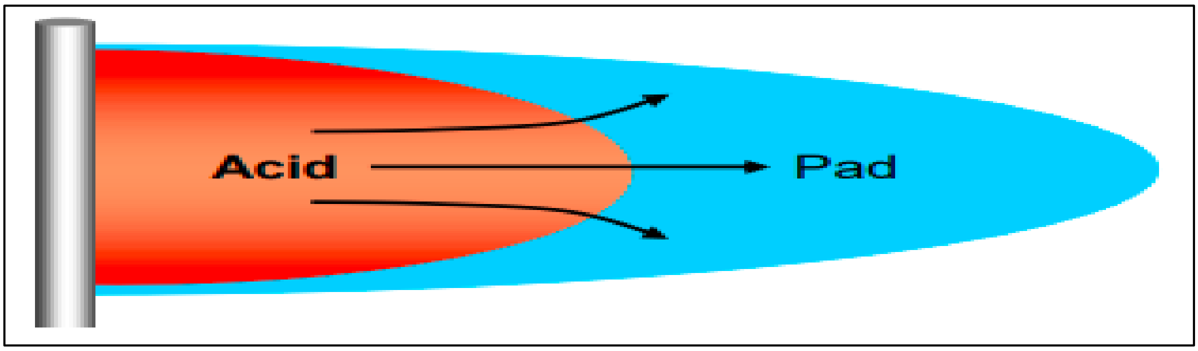

Figure II.6: Acid spending rate. **[24]**

II.7.3 Acid transport along fracture length

- Occurs when viscous fluid is displaced by less viscous fluid.
- Three positive effects:
  - Acid velocity is increased.
  - Acid etched length is increased. **[24]**

Figure (II.7) below shows acid transport along fracture length.

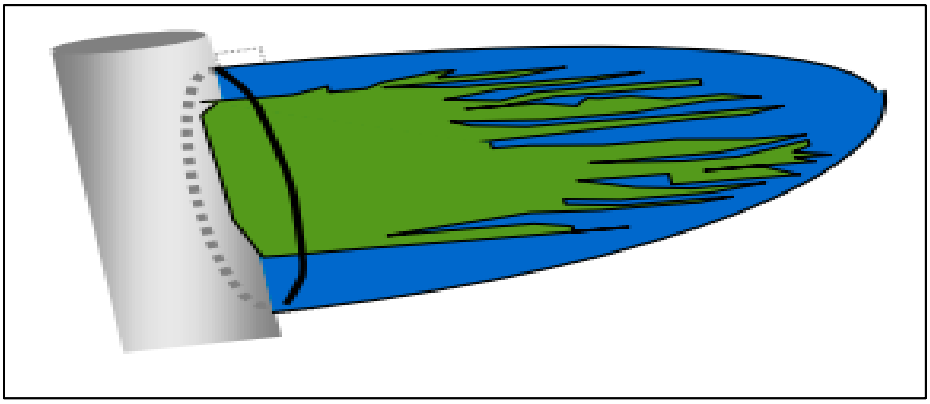

Figure II.7: Acid transport along fracture length. **[24]**

II.8 The effectiveness of acid fracturing treatment

The effectiveness of the acid fracturing treatment is largely determined by the length of the etched fracture.

Effective length of the fracture is determined primarily by two (2) factors:

- **Acid spending:** It's the rate that acid reacts with the formation. This etches the fracture face but also neutralizes acid until at some point, acid is reduced to salt water and no additional effective length can be achieved. The rate of acid spending at each point along the fracture face is controlled by two processes:
  - **Acid reaction rate (Rx):** Rx determines how fast acid molecules can react with carbonate rock on the fracture face.
  - **Acid mass transport:** This is the physical transport of acid molecules from the center of the fracture toward the fracture face. This can include both a molecular diffusion rate and convection for turbulent flow. **[23]**
- **Fluid loss:** For a propped hydraulic fracture, the rate of fluid loss at each point in the fracture tends to decrease due to the buildup of a viscous fluid bank in the formation and/or the placement of a gel filter cake on the fracture face. For acid fracture treatments, the opposite may be true. That is, as acid leaks off into the formation, it tends to continue dissolving rock and enhancing permeability. Thus, the rate of fluid loss at each place along the fracture face tends to increase with time causing acid treatments to generally experience very high fluid loss. **[23]**

II.9 Selecting acid fluids

There are many considerations for acid fracture treatments. These are the considerations:

- **Acid strength:** This is a function of the acid type and also the acid concentration (measured as a volume fraction, i.e..28% HCl). Acid strength is a measure of the "dissolving power." That is, how many pounds of carbonate can be dissolved by how many gallons of acid fluid? Thus, HCl is more efficient/economic in terms of pure dissolving power, but it also reacts much faster and thus may yield less acid-etched penetration. **[24]**
- **Acid Rx:** This defines how fast acid molecules combine with the carbonate molecules at the fracture face. For most formations, the Rx of HCl is essentially instantaneous, so this is not an important property. **[24]**
- **Acid mass transport:** This defines how fast acid molecules transfer from the middle of the fracture to the fracture face. **[24]**
- **Fluid loss control:** The viscosity of the acid fluid is an important parameter for controlling fluid loss since gelled acids cannot build a filter cake. **[24]**

II.10 Acid fracture conductivity

- Conductivity increases as etched width increases.
- Conductivity decreases as effective closure stress increases.**[23]**

II.11 Factors influencing half-length and conductivity

- **Acid leak-off:** Additional complication due to gel wormhole development.
- **Injection rate.**
- **Acid type, strength and volume:** Affects etched width and fracture lengths.
- **Acid viscosity:** Governs fracture width and acid transport along length.
- **Formation type:** Mineralogy, temperature, saturation, wettability. **[25]**

II.12 Acid fracturing design considerations

- Fracture propagation to the desired length.
- Acid is capable of dissolving large amount of reservoir rock.
- Retain adequate length and conductivity after closure.
- Rapid cleanup of treatment fluid.
- Cost effective. **[25]**

II.13 Acid fracturing fluids

II.13.1 OpenPath Reach (Retarded acid)

- **OPR concept**

OpenPath Reach is a single-phase retarded acid with high dissolution capacity. It's acid with a reduced reaction rate, it allows to penetrate more deeply into the fracture. The degree of retardation is defined by retardation factor (RF). Figure (II.8) represents OpenPath Reach penetration deep into the reservoir. **[25]**

Figure II.8: OpenPath Reach penetration deep into the reservoir.**[25]**

- **OpenPath Reach application**

OPR is applicable in acid fracturing and matrix stimulation treatments in carbonate formations.

- ➢ **Matrix acidizing**

In matrix stimulation, OpenPath Reach services create longer wormholes in comparison with treatments using unmodified hydrochloric acid. Because the fluid system is compatible with friction reducers, designs may include high-rate pumping to accommodate long intervals and further extend wormhole length. **[25]**

- ➢ **Acid fracturing**

For acid fracturing, OpenPath Reach services improve the conductive fracture length in comparison with treatments using the same volume of unmodified hydrochloric acid.

OpenPath Reach service designs may also include a high-viscosity pad fluid followed by the lower-viscosity single-phase fluid system. This viscosity difference promotes viscous fingering, which creates selective etching patterns that help to maintain open channels for hydrocarbon flow after fracture closure. **[25]**

- **OPR benefits**

- Increases production by delivering reactive treatment fluids deep into the reservoir.
- Reduces surface equipment requirements by using single-phase fluid systems.
- Improves logistics with simplified fluid systems.
- Limits environmental footprint compared with services using emulsified acid systems.**[25]**

- **OPR Features**

- Low-viscosity, single-phase retarded acid system with high dissolution capacity.
- Engineered job designs using the Kinetix* stimulation software suite.
- High-rate pumping option.
- Adjustable acid reaction rate for design flexibility to suit reservoir rock properties and conditions.
- Compatibility with OpenPath Sequence* diversion stimulation service and MaxCO3 Acid degradable diversion acid system. **[25]**

II.13.2 Viscoelastic diverting acid (VDA)

- **Viscoelastic diverting acid concept**

Viscoelastic diverting acid contains a unique chemical system that reduces the chance of forming a dominating wormhole during matrix acid treatments of carbonate reservoirs. The VDA blocks the growth of wormholes by temporarily forming a barrier in the wormholes by reducing the further loss of fluid into the wormholes. After the acidizing treatment, the barrier breaks down upon contacting producing hydrocarbons and the viscosity of spent VDA is greatly reduced.**[26]**

- **Viscoelastic diverting acid application**

- ➢ Stimulation of:
  - Oil and gas carbonate reservoirs.
  - Reservoirs with multiple layers, long production intervals, or permeability variation.
  - Horizontal and vertical wells.
- ➢ Multilayered and reservoirs with long production intervals.
- ➢ Bull-heading or pumping through coiled tubing. **[26]**

- **Viscoelastic diverting acid benefits**

- Self-diverting acid system.
- Operation as sole treating fluid or in combination with other fluids.
- Increased zonal coverage.
- No residual formation damages.
- Single treatment fluid for simplified operations.
- Easy fluid recovery and well cleanup.
- Solids- and polymer-free.
- Rated to 300 degF [149 degC].
- Rapid viscosity development on acid spending.
- Viscosity reduction on contact with hydrocarbon. **[26]**

II.13.3 MaxCO$_3$ Acid

- **MaxCO$_3$ Acid concept**

MaxCO$_3$ acid is degradable diversion acid system combines VDA (viscoelastic diverting acid) and degradable fibers. It is designed to temporarily block or decrease leak-off into natural fractures and wormholes in carbonate reservoirs by creating fiber bridges in the natural fractures, and increasing viscosity as the acid spends. In acid fracturing applications, MaxCO$_3$ acid reduces leak-off in fissures and natural fractures. **[27]**

- **MaxCO$_3$ acid application**

- Reservoirs with high permeability contrasts and/or natural fractures.
- Bottomhole temperatures between 175 and 250 degF [79 and 121 degC].
- Carbonate oil or gas wells.
- Open hole or cased hole intervals, regardless of deviation. **[27]**

- **MaxCO$_3$ acid benefits**

- Degrades completely, eliminating risk of costly cleanout interventions.
- Targets permeability contrasts, allowing superior zonal coverage.
- Effectively controls leak off.
- Requires lower treatment volumes and less well cleanup time. **[27]**

- **MaxCO$_3$ acid features**

- Diverts effectively at low treatment rates.
- Continues to stimulate as it degrades.
- Can be bullheaded or pumped through CT.

- Can be pumped with most common acid stimulation systems.
- Can be batch mixed for small volume jobs or mixed on the fly for larger treatments.**[27]**

II.13.4 Hydrochloric Acid

- **Hydrochloric Acid concept**

Hydrochloric acid (HCl) is a solution of hydrogen chloride (HCl) gas in water. The strength of the acid depends on how much HCl gas is dissolved in a given quantity of water. Maximum concentration of commercial grade HCl is about 36% by weight. Concentrations of HCl up to 28% by weight are generally used in oilfield treatments.**[28]**

- **Reaction of HCl with carbonate formation**

When HCl is pumped into a carbonate formation (limestone or dolomite), a chemical reaction takes place producing calcium chloride ($CaCl_2$), carbon dioxide (CO_2) and water (H_2O).**[28]**

This reaction is represented by the following equations:

HCl with limestone reaction

$$2HCl + CaCO_2 \rightarrow CaCl_2 + CO_2\uparrow + H_2O$$

HCl with dolomite reaction

$$2HCl + CaMg\,(CO_3)_2 \rightarrow CaCl2 + MgCl_2 + CO_2\uparrow + H_2O$$

- **Different acid types and strengths**
- **Different acid types**

The most common acid used in the oilfield for acid fracturing is hydrochloric acid (HCl). HCl is a strong mineral acid. The usual HCl concentrations in acid fracturing are 15, 20 and 28%.

Weak organic acids such as formic (HCOOH) and acetic (CH_3COOH), are also used. The dissolving power of organic acids is much lower than that of HCl. these organic acids should be used at concentrations above 9% (formic) or 10% (acetic) because, when spent, high concentrations of organic calcium salts may precipitate in the formation.[**29]**

Formic Acid with carbonate reaction:

$$CaCO_3 + 2\,HCOOH \rightarrow H_2O + CO_2\uparrow + Ca\,(HCOO)_2 \text{ (Calcium formate)}$$

Acetic Acid with carbonate reaction:

$$CaCO_3 + 2\,CH_3COOH \rightarrow H_2O + CO_2\uparrow + Ca\,(CH3COO)_2 \text{ (Ca acetate)}$$

- **Different acid strengths**

HCl is a strong mineral acid and organic acids (formic& acetic acid) are weak acids.

Table (II-2) shows different acid type and strengths.

Table II.2: Different acid type and strengths. **[24]**

Dissolved Acid Type (100oF)	**Strength (%)**	**$CaCO_3$ Dissolved (lb/1000 g)**
Hydrochloric	**15** **20** **28**	**1833** **2515** **3662**
Formic	**9**	**726**
Acetic	**10**	**422**

II.14 Conclusion

Acid fracturing is stimulation technique used in both limestone and dolomite reservoirs. It is achieved by using acid and different additives including retarded agent.

Chapter III:

Comparison study of OPR & HCl

Chapter III: Comparison study of OPR & HCl

III.1 Introduction

Acid fracturing has been the preferred alternative stimulation method in carbonate formations in which acid. The acid used is HCl but it has insufficient results. This circumstance can be explained by unachieved planed fracture geometry parameters and low retained fracture conductivity due to the fast reaction of HCl with the carbonate and doesn't penetrate to the desired distance. HCl is combined with retarded agent (OpenPath Reach) to ensure a long penetration of the acid and to give better results during the acid fracturing operation. OpenPath Reach is a retarded acid with high dissolution capacity, it reduces reaction rate and allows to penetrate more deeply into the fracture.

III.2 Problematic description

Acid fracturing is a stimulation process in which acid, usually hydrochloric acid (HCl), is injected into a limestone or dolomite formation at a pressure sufficient to fracture the formation or to open existing fractures. As the acid flows along the fracture, portions of the fracture face are dissolved. Since flowing acid tends to etch in a non-uniform manner, conductive channels are created which usually remain open after the fracture closes. **[29]**

The effectiveness of the acid fracturing treatment is largely determined by the length of the etched fracture. As with conventional hydraulic fracturing operations, the principal objective of an acid fracturing treatment is to provide a conductive fracture with sufficient length to allow efficient drainage of the reservoir. Acid fracturing relies upon acid-etched fracture faces to provide the necessary conductivity.

During the injection of the HCl acid, it reacts immediately with the formation and for this reason using OPR technology to retard the reaction of the acid with the formation to ensure a long penetration of the acid and gives better results and a best recuperation of the hydrocarbons.

In this study a comparison between HCl and retarded agent will be studied including laboratory experiments.

- What is the difference between acid fracturing with and without retarded agent?

III.3 Objective

Main objectives of this experience are:

1- Perform series of experiments in the laboratory to obtain experimental data for study the performance of retarded agent and compare HCl with OPR

2- Determine the solubility of carbonate in different percentage of HCl for different temperature.

3- Determine the effect of retarded agent on the concentration of the acid.

4- Determine solubility of carbonate in different percentage of HCl using constant quantity of retarded agent.

5- Determine solubility of carbonate in OPR at different temperatures.

By achieving the above objectives, this research allows to know the performance of retarded agent and compare the HCl acid with retarded agent.

III.4 Methodology

III.4.1 Materials & Products

III.4.1.1 Products

- **HCl acid**

Hydrochloric acid is usually prepared industrially by dissolving hydrogen chloride in water .It is classified as a strong acid. Bulk industrial-grade is therefore 30% to 35%, optimized to balance transport efficiency and product loss through evaporation. Hydrochloric acid is used for a large number of small-scale applications such as oil production for stimulation by injecting hydrochloric acid into the rock formation of an oil well, dissolving a portion of the rock, and creating a large-pore structure. Hydrochloric acid has been used for dissolving calcium carbonate.**[30]**

Figure III.1: 33%HCl Acid. **[32]**

Retarded agent

The OpenPath Reach acid retardation package consists of two components:

- **First component:** reduces the diffusion of hydrogen ions in the acid, meaning that the transport of protons to the surface of the formation is slowed down, effectively decreasing the dissolution rate of the rock by HCl.**[31]**
- **Second component:** diminishes the rock contact surface of hydrogen ions, which prevents HCl from easily reacting with the formation. **[31].**

Figure III.2: Retarded agent additives. **[32]**

Calcium carbonate ($CaCO_3$)

It is a chemical compound. It is a white insoluble powder, it's the principal compound of carbonate formation.

Figure III.3: $CaCO_3$ & Cement samples. **[32]**

- **Additives**

- **Cement:** a dry powdery substance.
- **Corrosion inhibitor and inhibitor aid:** it is a chemicals substance that reduces the corrosion rate of a metal surface exposed to corrosion.
- **Iron reducing agent:** it is a compound that is capable of reducing or removing iron from a chemical or biological system.

Figure III.4: Additives. **[32]**

III.4.1.2 Materials

- **pH meter**

It is a tool used to measure pH. It also allows the temperature to be measured simultaneously.

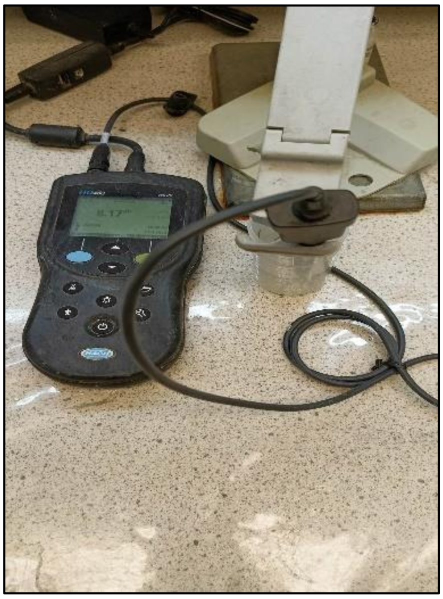

Figure III.5: pH meter. **[32]**

➢ Water-bath

Water bath is a laboratory equipment filled with heated water. It is used to incubate samples in water at determined temperature.

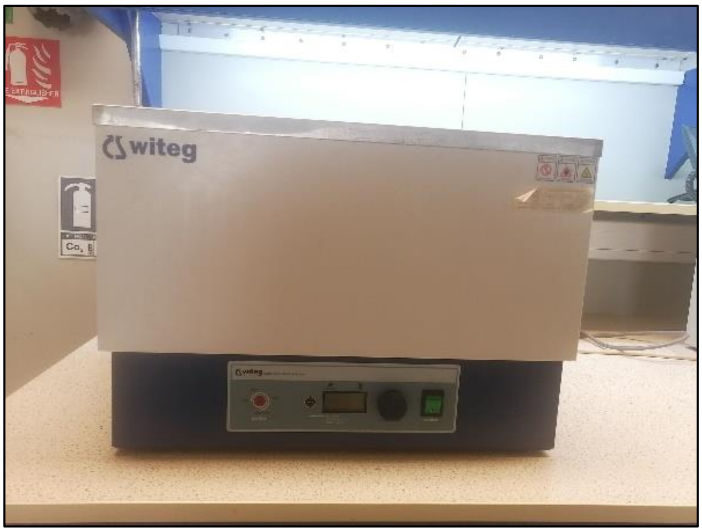

Figure III.6: Water-bath. **[32]**

➢ Acid-base titration instrument

Acid-base titration instrument is used to determine concentration of sample of acid or base and carried to use a burette.

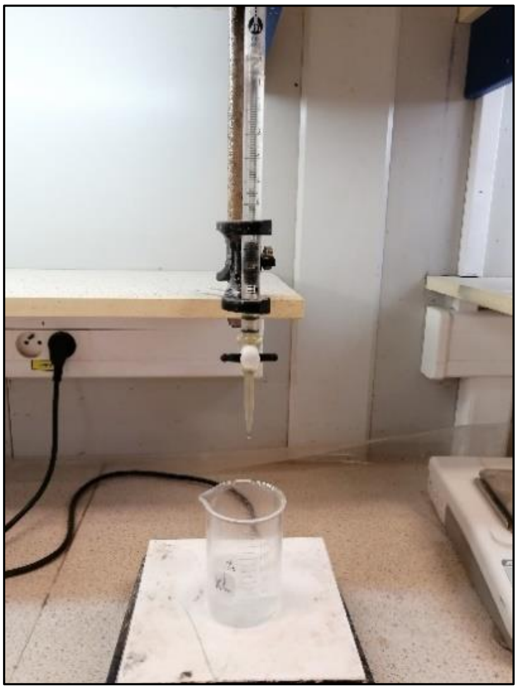

Figure III.7: Acid-base titration instrument. **[32]**

III.4.2 Preparation procedures

The tests have been conducted in slb fracturing laboratory with all chemicals that have been used in the field. Below is the general mixing procedure:

III.4.2.1 Preparation of samples

- Prepare the required volume of water.
- Add calcium carbonate ($CaCO_3$).
- Add cement.
- Mix using a Waring Blender, and immediately pour the sample into a container.
- Put the samples in the oven at 90degC at least for 2hours and allow them to dry.

Figure III.8: $CaCO_3$ samples. **[32]**

III.4.2.2 Preparing 15%HCl & OPR 15%

- **Preparation of 15%HCl**

- Mix total required water.
- Add iron reducing agent.
- Add corrosion inhibitor and inhibitor aid.
- Add the required amount of concentered acid HCl.

Figure III.9: 15% HCl solution. **[32]**

- **Preparation of OpenPath Reach (OPR) 15%**

1. Mix the total required retarded agent I with half planned water.
2. Measure specific gravity.
3. Add half of required amount of corrosion inhibitor and inhibitor aid.
4. Add Iron reducing agent.
5. Add the required amount of concentered acid (HCl).
6. Add the remaining half water.
7. Titrate the sample using the titration method, and calculate the acid concentration of acid.
8. Add the remaining half of corrosion inhibitor and inhibitor aid.
9. Add retarded agent II and F_{103} and allow them to mix.
10. Measure the specific gravity.

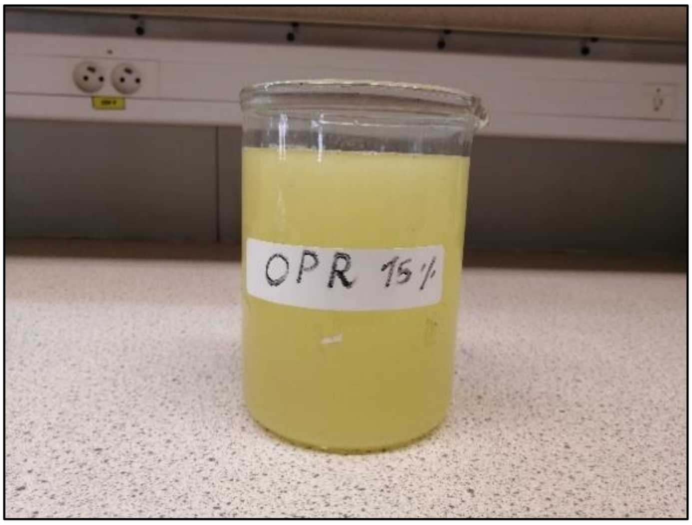

Figure III.10: OPR 15% solution. **[32]**

- **Application**

- Put samples of same weight in the oven at temperature 88°C.
- Take the same volume of OPR and HCl.
- Put the heated samples in the solution.
- Put them in the oven again at T=88°C for 6 hours.
- Measure the weight of samples after every 1 hour.

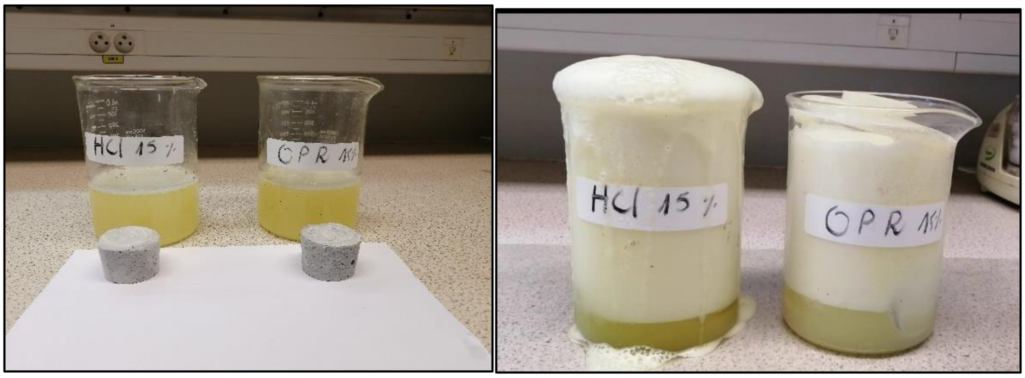

Figure III.11: The reaction of the samples on 15%HCl & OPR 15%.**[32]**

III.4.2.3 Preparing HCl &OPR for different concentrations

- **Preparing HCl for different concentrations**

- Follow the same steps as we prepared 15%HCl and just change the volume of water and HCl used.
- Put samples in different concentration of HCl of same volume and let them on water bath for one hour in different temperatures.
- Measure their weight after every 15 min.

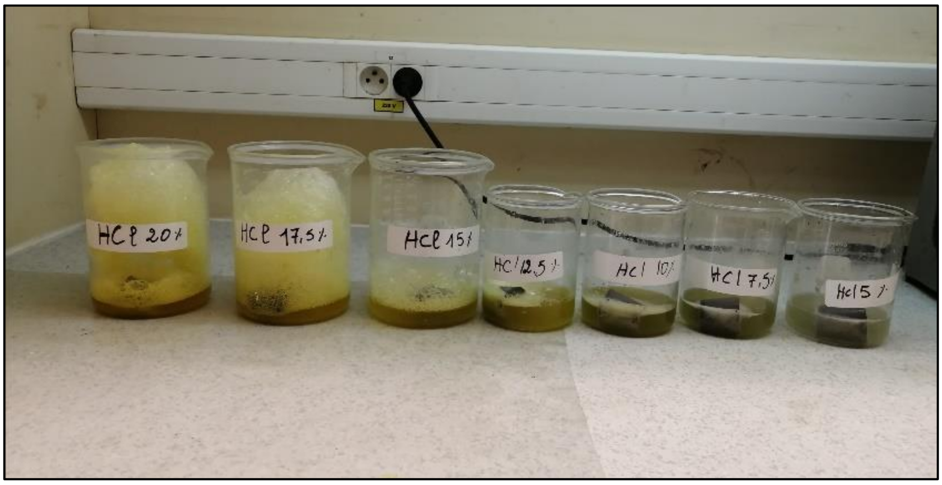

Figure III.12: The reaction of the samples on different concentrations of HCl. **[32]**

- **Preparing OPR for different concentrations**

- Flow the same steps as we prepared OPR 15% and just we change the volume of water and HCl used.
- Add the same weight of retarded agent additives to all concentrations of HCl with taking the reference the weight of retarded agent in OPR 15% to study the effect of different concentration on it.

- Put the samples at different concentrations of OPR using the same volume and keep themin the water bath for one hour at T=88C°.
- Put samples on same volume of OPR 15% at different temperatures.
- Measure their weight after every 15 min.

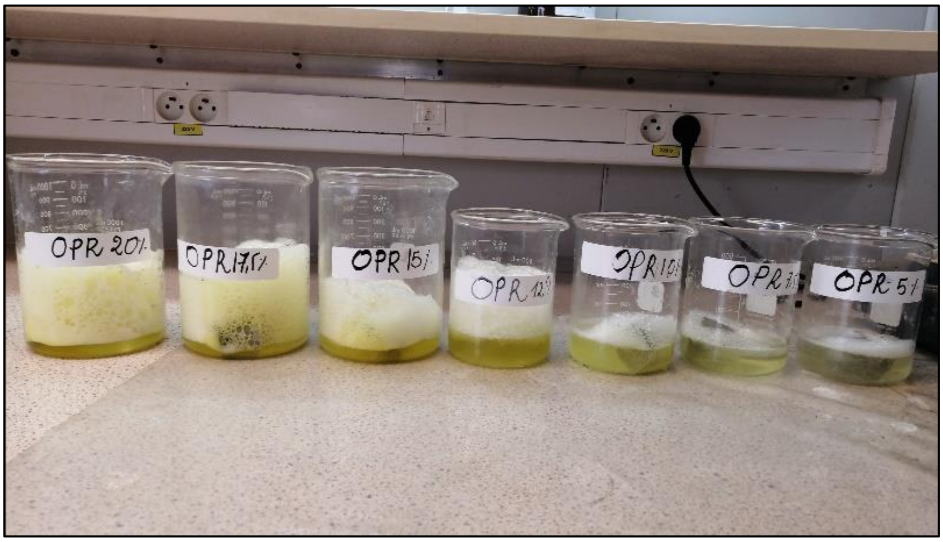

Figure III.13: The reaction of the samples on different concentrations of OPR. **[32]**

III.4.2.4 Titration

To confirm the effect of retarded agent on the concentration of acid by using titration method we have to:

- Take around 0.7 g of acid sample and adding 50 ml of distilled water.

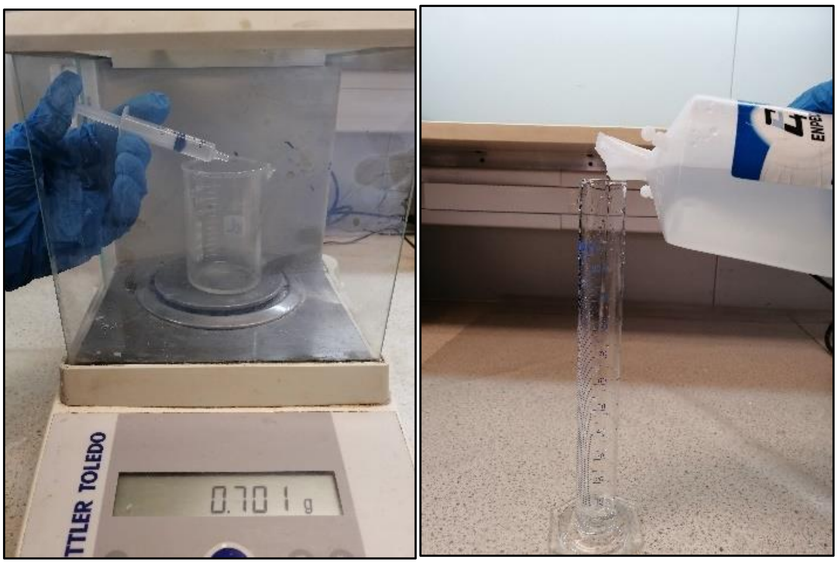

Figure III.14: Acid sample &Distilled water. **[32]**

- Add phenolphthalein

Figure III.15 : phenolphthalein. **[32]**

- Then titrate with NaOH tell get a pink color.

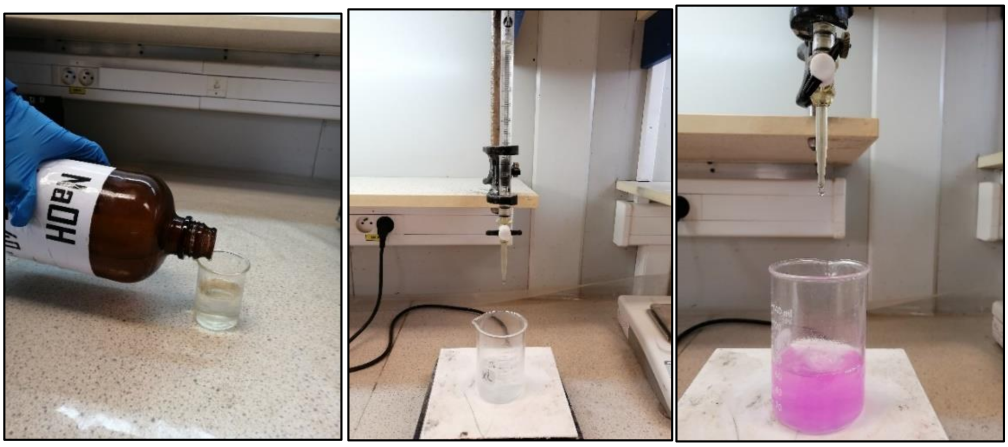

Figure III.16: Acid titration with NaOH. **[32]**

- Reading the volume of NaOH and calculate the concentration of acid by using an equation or a program.

III.5 Results & Discussions

III.5.1 Comparison of retarded agent performed in 15% HCl at T=88C°

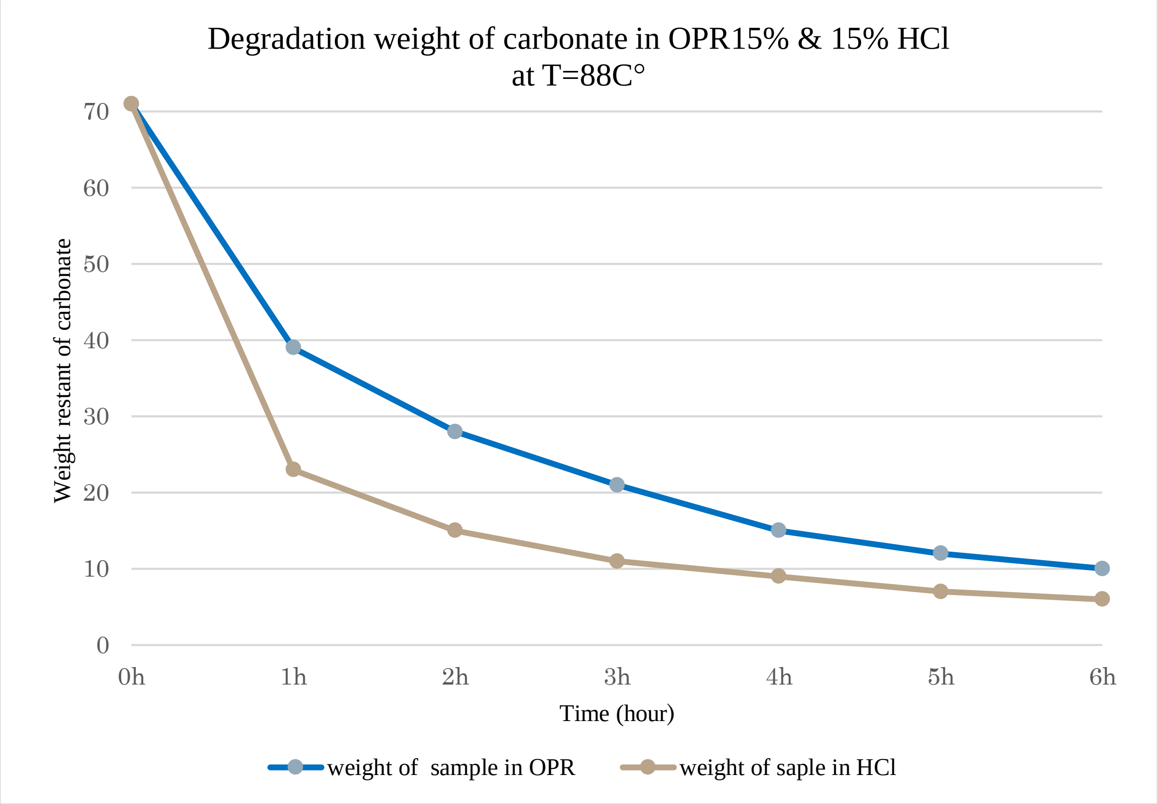

Figure III.17: Weight degradation of carbonate in OPR 15% &15%HCl at T=88C°.

Figure (III.17) represents the weight variation of two carbonate samples emerged in HCl and OPR in function of time. The weight of carbonate samples decreases fast more in HCl than OPR. The weight of the two samples were the same around 71g in t=0.The graph shows that after one hour the weight of samples decreases to 23g in HCl and to 39g in OPR. The weight of the sample emerged in the HCl decreases fast more than the weight of the sample emerged in the OPR.

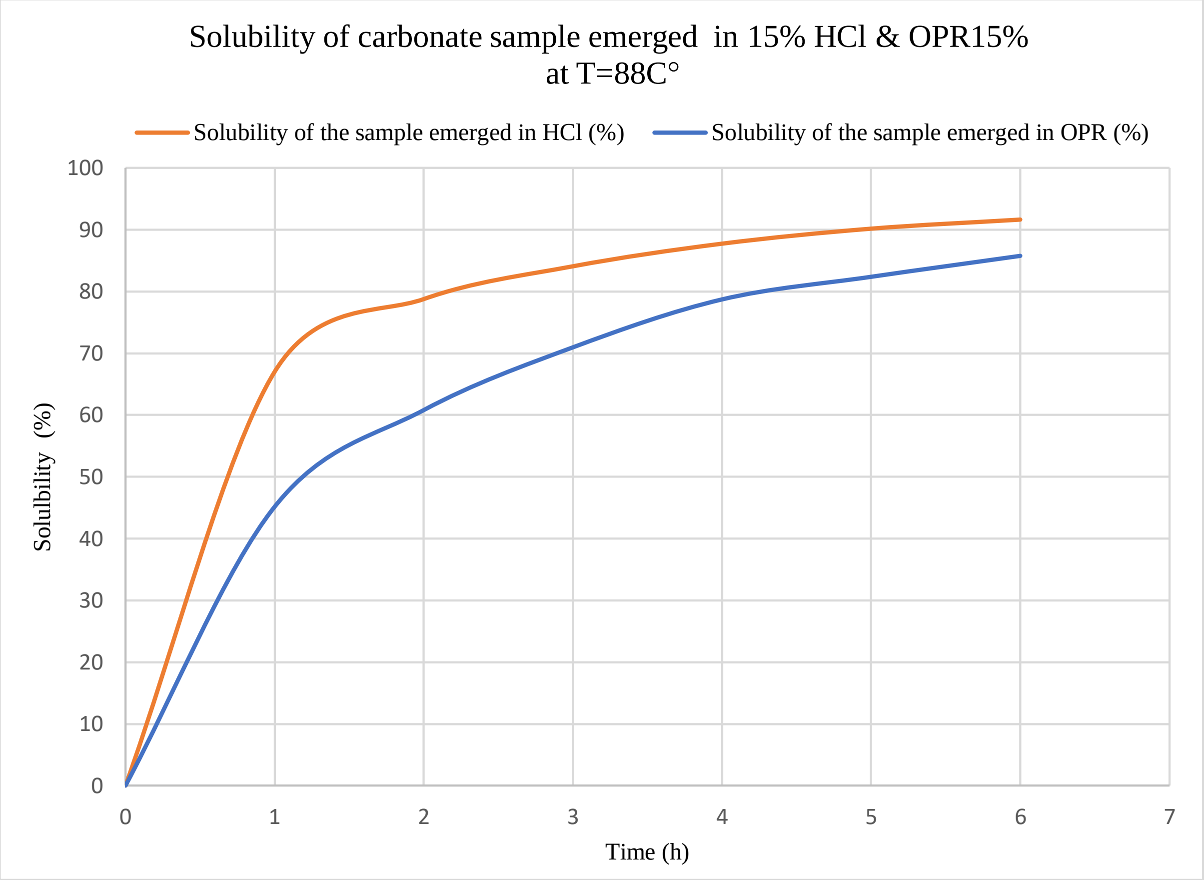

Figure III.18: Solubility of carbonate samples weight in OPR 15 % & 15%HCl.

Figure (III.18) shows the solubility of carbonate samples weight emerged in OPR 15% & HCl 15% in percentage (%) in function of time. The solubility of the carbonate in HCl 15% is fast more than solubility of the carbonate sample in the OPR 15%. The solubility of the carbonate in HCl 15% after one hour is around 67% and in the OPR 15% reaches 46%.

III.5.2 Effect of HCl concentration on carbonate solubility at different temperatures

- **Result at 66C°**

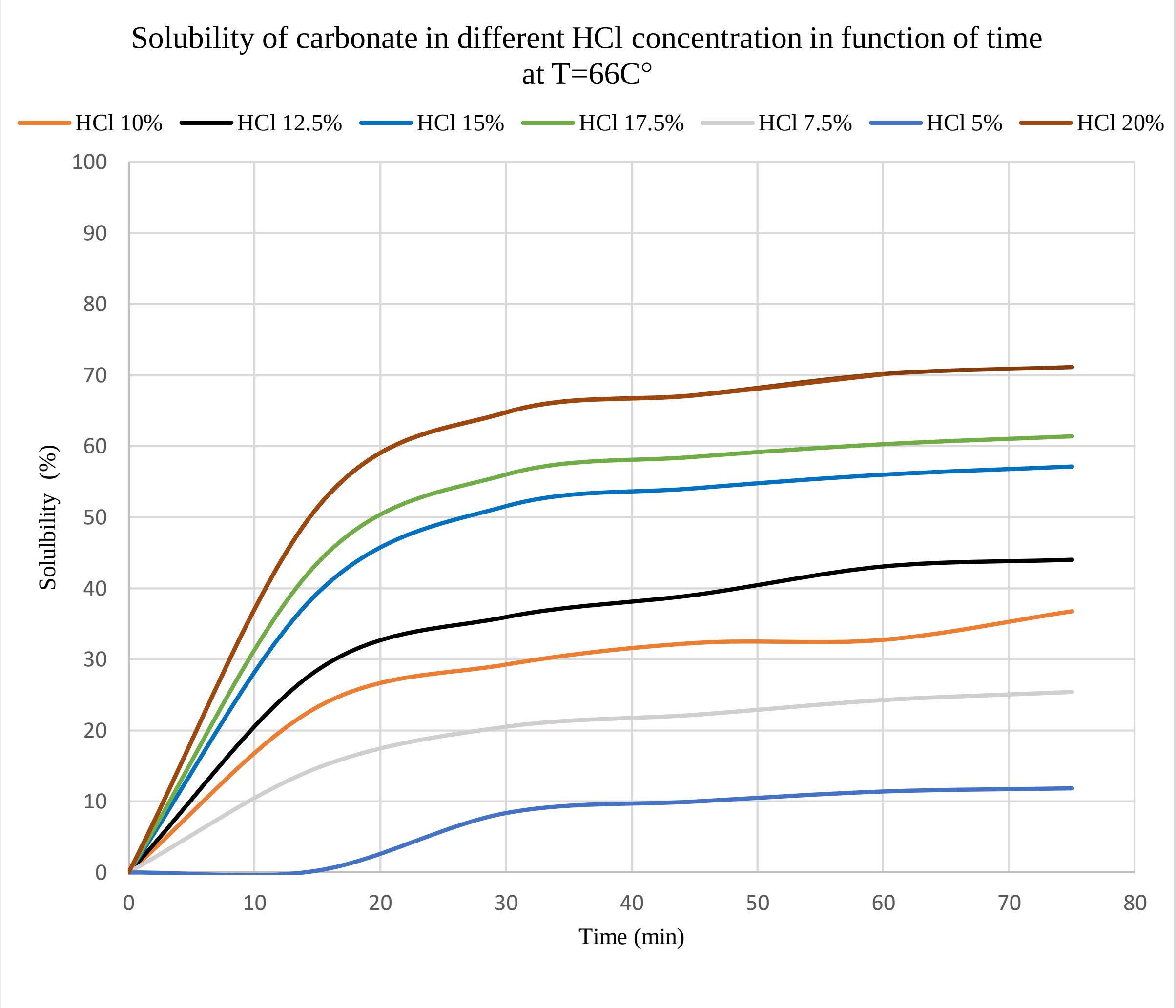

Figure III.19: Solubility of carbonate in different HCl concentration at T=66C°.

Figure (III.19) represented below shows the solubility of carbonate samples in different HCl concentration in function of time at T=66C°.The graph shows that the solubility increases with the augmentation of HCl concentration. Each concentration gives a different degree of solubility as it's represented the solubility of the carbonate in HCl 5% is about 11% after 75min and 25% in HCl 7.5%, 37% in HCl 10%, 44% in HCl 12.5%, 57% in HCl 17.5% and 71% in HCl 20%.

Table III.1 represents pH of different acids after 75min at T=66C°.

Table III.1: pH of different acids after 75min at T=66C°.

HCl (%)	5%	7.5%	10%	12.5%	15%	17.5%	20%
PH	**1.4**	**0.9**	**0.6**	**0.4**	**0.0**	**-0.3**	**-0.7**

- **Result at 75C°**

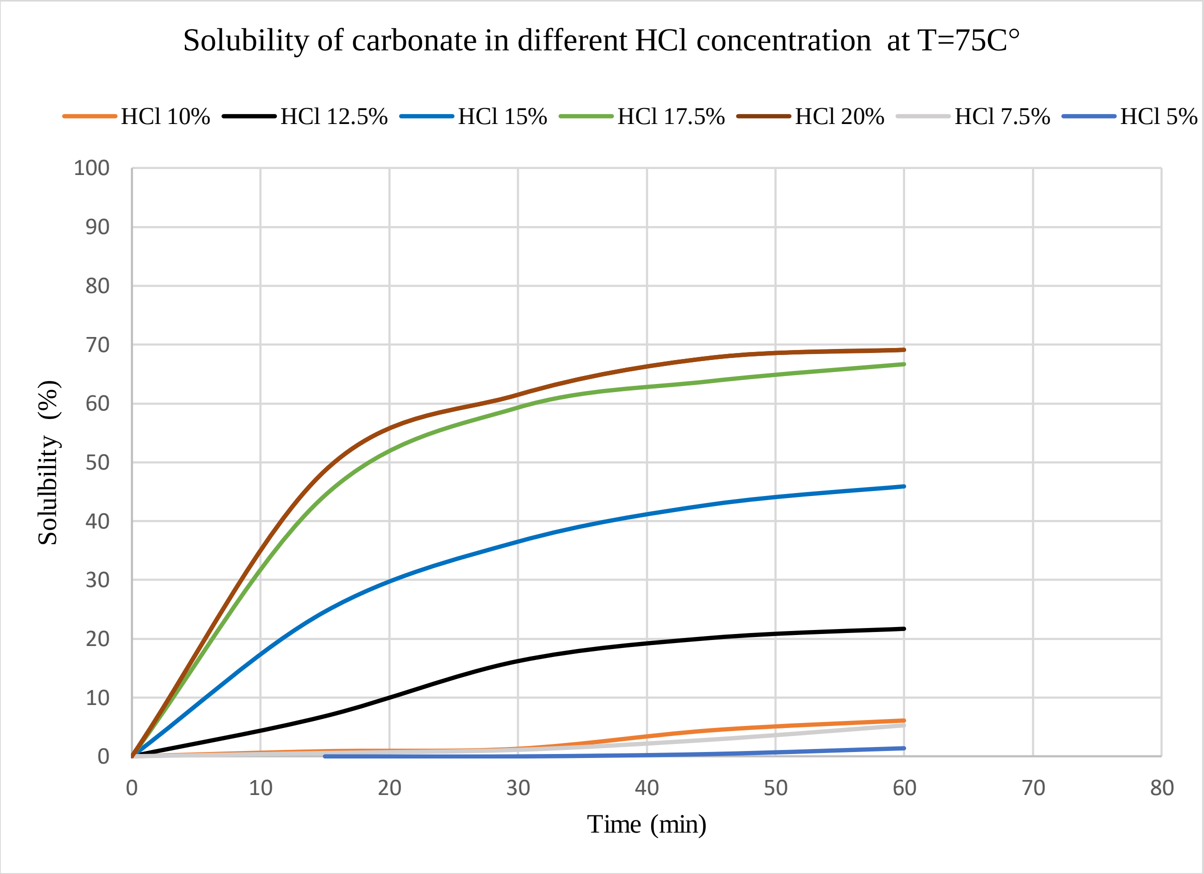

Figure III.20: Solubility of carbonate in different concentration of HCl at T=75°C.

Fig III.20 represents a chart of solubility of carbonate samples in different HCl concentration in function of time at T=75°C.The solubility increases with the augmentation of HCl concentration. This graph shows that the solubility in heigh concentration is increased by the increasing of the temperature and the solubility diminish with the augmentation of temperature with low concentrations.

Table III.2 represents pH of different acids after 75min at T=75°C.

Table III.2: pH of different acids after 75min at T=75°C.

HCl (%)	**5%**	**7.5%**	**10%**	**12.5%**	**15%**	**17.5%**	**20%**
PH	**0.9**	**0.5**	**0.3**	**0.2**	**-0.2**	**-0.4**	**-0.9**

- **Result at 88C°:**

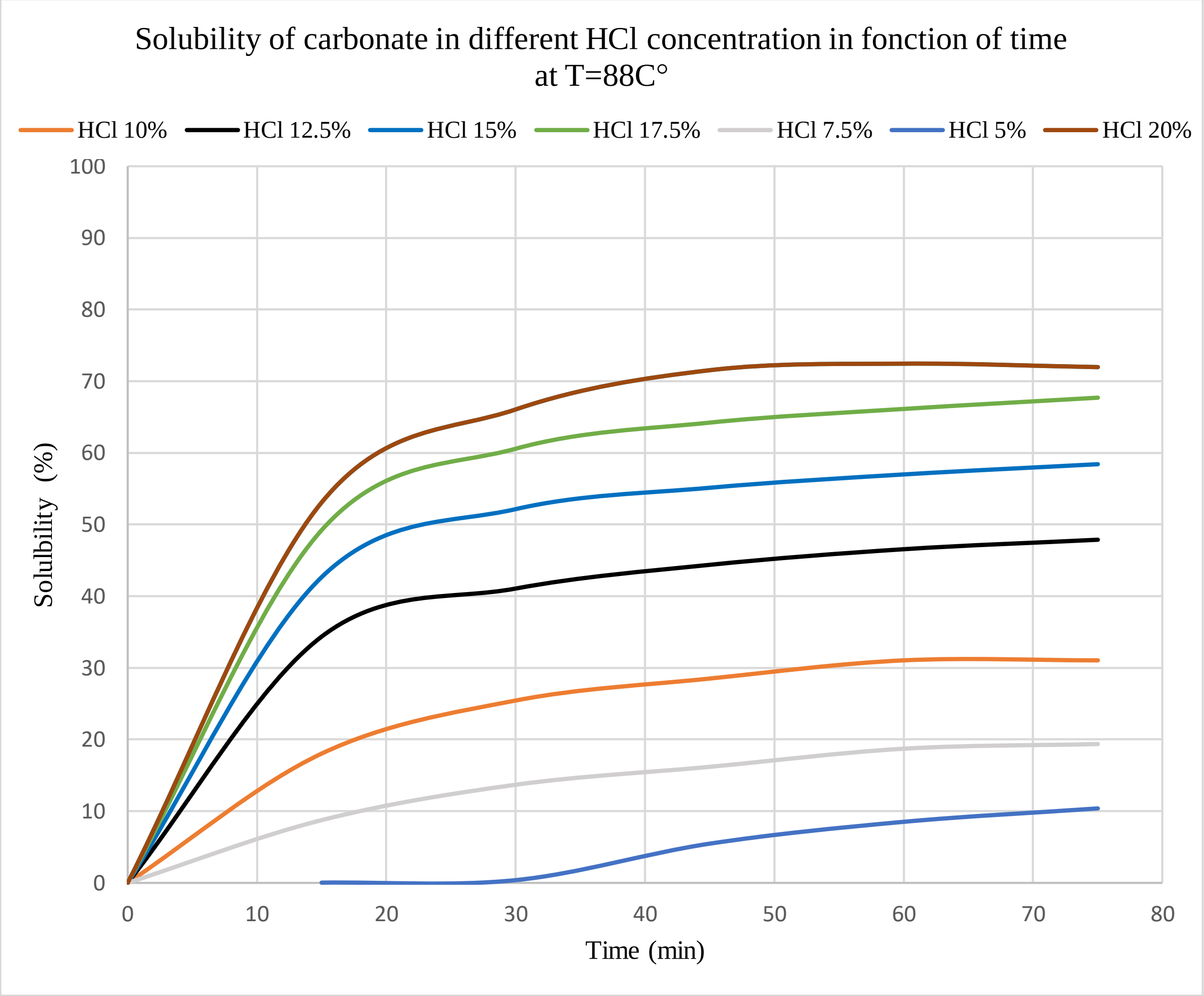

Figure III.21: Solubility of carbonate samples in different HCl concentration at T=88C°.

Figure III.21 represents a chart of solubility of carbonate samples in different HCl concentration in function of time at T=88C°.The solubility increases with the augmentation of HCl concentration. This graph shows also that the solubility in heigh concentration is increased by the increasing of the temperature and the solubility diminish with the augmentation of temperature with low concentrations.

Table (III.3) represents pH of different acids after 75min at T=88C°.

Table III.3: pH of different concentration HCl at T=88C°.

HCl (%)	**5%**	**7.5%**	**10%**	**12.5%**	**15%**	**17.5%**	**20%**
PH	**1.1**	**0.6**	**0.3**	**0.2**	**-0.1**	**-0.2**	**-0.6**

- **Result at 100C°:**

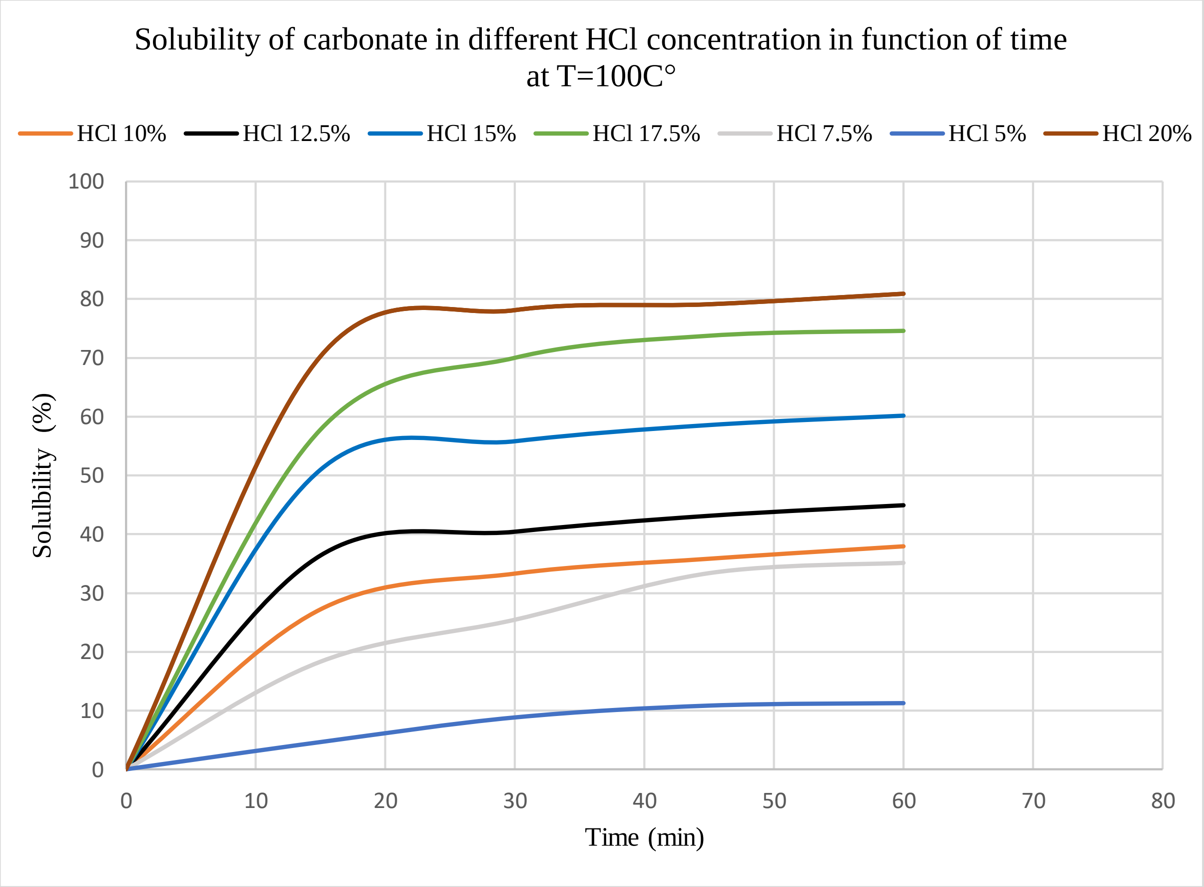

Figure III.22: Solubility of carbonate samples in different HCl concentration at T=100C°.

Figure (III.22) shows solubility of carbonate samples in different HCl concentration in function of time at T=100C°.The solubility in this temperature is very heigh that means the rate of reaction is increased by temperature, in t=60min the solubility in 20% HCl was 80.87%.

These different graphs (Fig III.22, Fig III.21, Fig III.20, Fig III.19), indicate that the solubility increases with the augmentation of temperature for heigh concentrations that means the rate of the reaction is decreased. The solubility decreases with the augmentation of temperature in low concentrations of acid (for T=66,75and 88C°).

The percentage of solubility observed was stable in 15%HCl with different temperatures.

Table (III.4) represents pH of different acids after 60 min at T=100C°.

Table III.4: pH of different acids after 60 min at T=100C°.

HCl (%)	**5%**	**7.5%**	**10%**	**12.5%**	**15%**	**17.5%**	**20%**
PH	**1.5**	**0.9**	**0.6**	**0.2**	**-0.3**	**-0.4**	**-0.9**

III.5.3 Effect of retarded agent at different HCl concentrations on carbonate samples

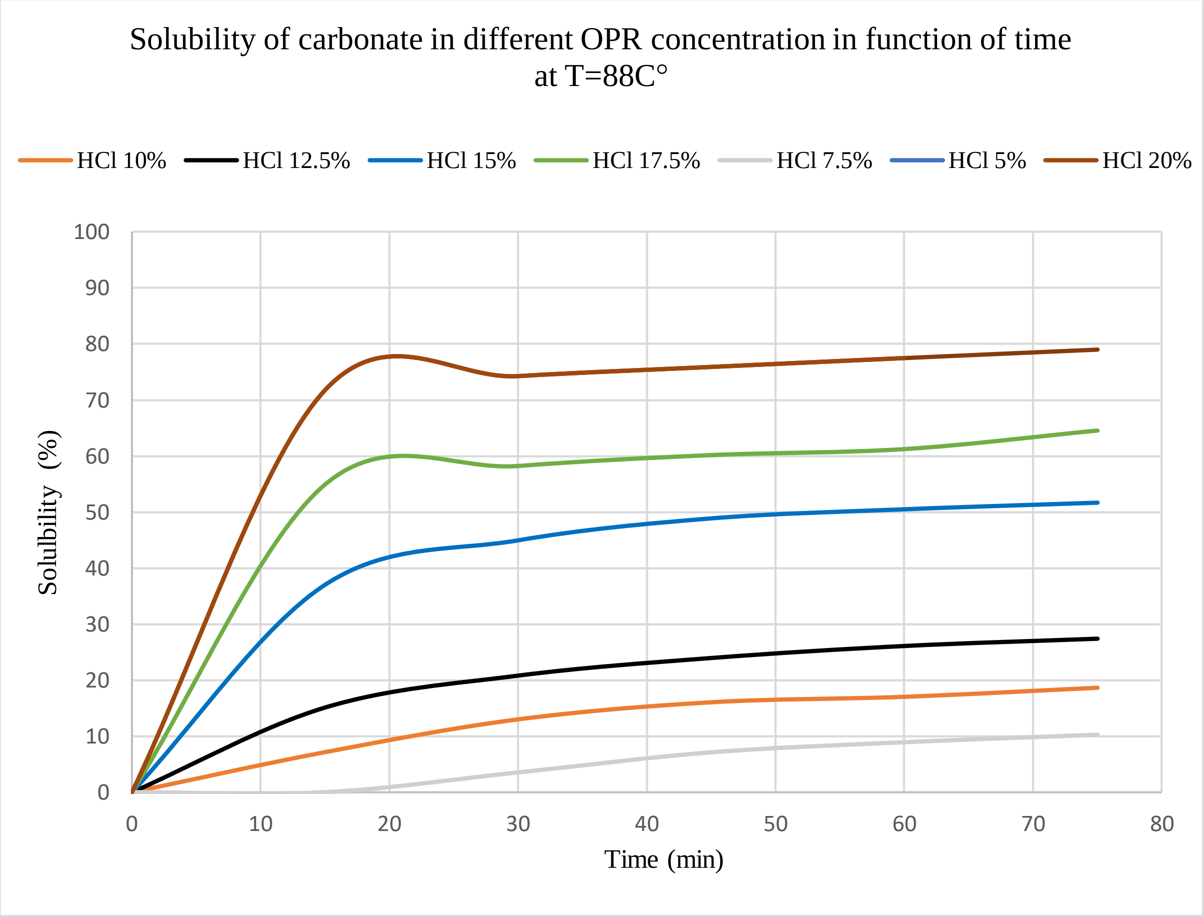

Figure III.23: Solubility of carbonate samples in different OPR concentration at T=88C°.

Figure III.23 represents the solubility of carbonate samples in different OPR concentration at T=88C°.The degree of solubility depends of the rate of concentration, as the concentration goes up the solubility augments.

By comparing the solubility in figure III.21 which represents the solubility of carbonate samples in different HCl concentration at T=88C° and figure III.23, it's noticed that the solubility in HCl with different concentrations is higher than the solubility in OPR with different concentrations that means the retarded agent retards the rate of rection.

In OPR 20%, the solubility percentage of carbonate sample was higher than the one in 20%HCl.

Table (III.5) shows pH of different OPR concentrations after 75 min at T=88C°.

Table III.5: pH of different OPR concentrations after 75 min at T=88C.

HCl (%)	**5%**	**7.5%**	**10%**	**12.5%**	**15%**	**17.5%**	**20%**
PH	**/**	**0.7**	**0.6**	**0.3**	**-0.4**	**-0.5**	**-0.6**

III.5.4 Effect of temperature on retarded agent performance:

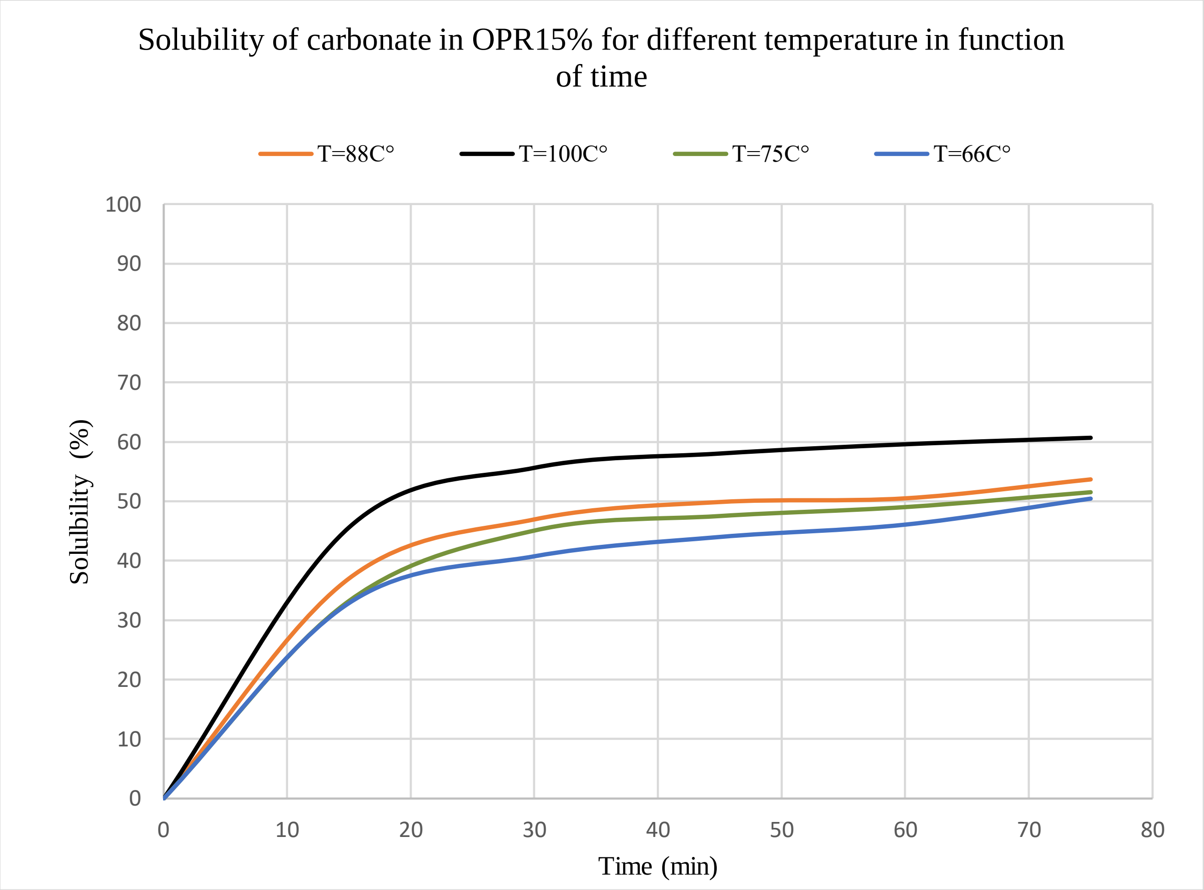

Figure III.24: Solubility of carbonate in OPR 15% at different temperatures in function of time.

Figure (III.28) represents the solubility of carbonate in OPR 15% at different temperatures in function of time. The solubility is close to each other and there is not a big difference in solubility at T=66C°, T=75C°, T=88C°, so the retarded agent retards the reaction with same rate at those temperatures.

The solubility in T=100C° is heigh and fast so the retarded agent didn’t work in this temperature.

III.5.5 Calculation of the concentration of acid after adding retarded agent

The concentration of OPR 5% is calculated using a program and the result gives 5.2% after adding retarded agent to the 5%HCl acid.

III.6 Case of study: Field “A”

III.6.1 Well information

The well was completed with a multistage hydraulic fracturing system (StageFRAC) and 4 ½” liner along the 1800 ft horizontal section. This multistage stimulation treatment included 9 acid fracturing stages pumped through 5” tubing. Reservoir pressure was 2400 psi and BHT 170 degF. Initial production estimated by 1200bbls/day. **[33]**

III.6.2 Challenge

- Long horizontal section.
- Initial low productivity with historical unsuccessful prop frac treatments.
- Long etched half-length required to maximize productivity. **[33]**

III.6.3 Solution

- OpenPath Reach with 20% HCl proposed as retarded acid system to treatment penetration.
- MaxCO_3 as main diverter. **[33]**

III.6.4 Field execution

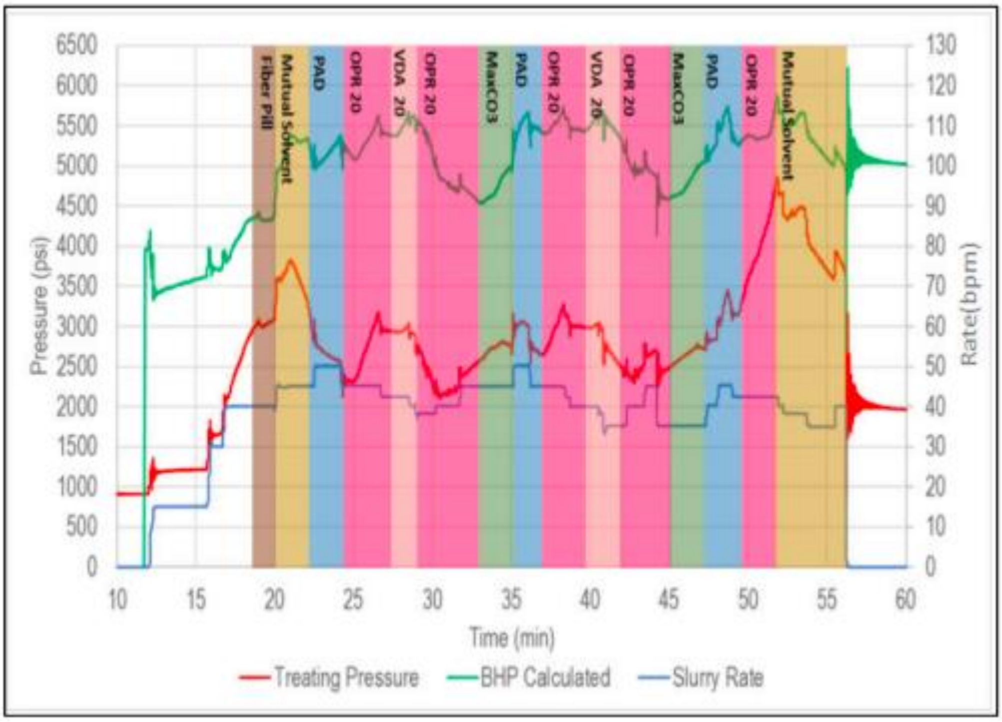

Figure III.25: Pumping plot. **[33]**

To increase the treatment and diversion effectiveness, stages are designed to be executed. Figure (III.31) shows one of the stages treatment plots. This stage included two $MaxCO_3$ stages that promoted bottom hole pressure increases of 486 psi and 469 psi respectively when entering the formation, 5 stages of OpenPath Reach 20, 3 stages of PAD and two stages of VDA. Although, BHP is calculated from surface pressure, the results obtained indicates effective diversion was achieved.

III.6.5 Production results

After acid fracturing treatment the initial production test for this well reported 3056 bbls/day, becoming the highest producer in the area. **[33]**

III.7 Conclusion

In this last chapter, a series of experiments have been performed to study the performance of retarded agent in acid fracturing technique.

The results that obtained are:

-Retarded agent reduces the reaction rate of HCl with the carbonate for this reason the solubility of the carbonate in the HCl is fast in the OPR. OpenPath Reach ensure less rapidity of rection what means more penetration of acid in frac.

- The rate of solubility of the carbonate depends of the degree of concentration of acid as the concentration goes up the solubility increases.

-The low concentrations of acid react in low temperature and decrease when temperature increase until the boiling temperature (100°C) where its rate of reaction increases again.

-The retarded agent has the same performance in different concentration of acid for different temperatures below the boiling temperature where it loses its performance.

-15%HCl is the concentration which keeps the same rate of reaction with all the temperatures and gives the best performance.

-The retarded agent doesn’t change the concentration of the acid.

General Conclusion & Recommendation

Acid Fracturing technique is a well stimulation technique used in carbonate formations. The first application of this technique in Algeria performed by Schlumberger in December 2022. The effectiveness of the acid fracturing treatment is largely determined by the length of the etched fracture. The problem of injection of the HCl acid, it reacts immediately with the formation and for this reason slb adds retarded agents to retard the rate of the reaction of the acid with the formation to ensure a long penetration of it and gives better results and a best recuperation of the hydrocarbons.

The objective of this project was to study the performance of retarded agent in acid fracturing technique to prove the efficiency of this retarded agent in acid fracturing technique.

In slb laboratory an experimental study carried out in this research project have shown the performance of retarded agent, the effect of HCl concentration on carbonate solubility at different temperatures, the effect of retarded agent at different HCl concentration on carbonate solubility, the effect of temperature on retarded agent performance and the effect of the retarded agent on the concentration of the acid.

This experimental study gave the following results:

- The retarded agent retards the rate of reaction of the acid, after one hour the solubility of carbonate in OPR is 45% and the solubility of the carbonate in the HCl is 67%.
- The acid with concentration of 15% has the best performance, it gives a range of solubility between 45% and 60% at temperature 66C°,75C°,88C° and 100C° after one hour.

In the case study on the well A, it confirms the effectiveness of the OpenPath Reach after adding retarding agent to the acid and the rate of recuperation for this well reported 3056 bbls/day.

Recommendations

Multiple laboratory tests were performed in slb laboratory to investigate the performance of stimulation of retarded in different conditions.

The obtained results helped to give the following recommendations:

- Retarded agent is recommended for 15% to achieve more reaction in the carbonate formation.
- More attention is needed when using retarded agent at higher temperatures.
- Recommended to perform lab tests like:
    - Solubility of test with rock sample at different other temperature.
    - Solubility of test with rock sample at different other concentrations.
    - Compatibility and emulsion tests between acid systems and the oil formation with live and spent acid are recommended.

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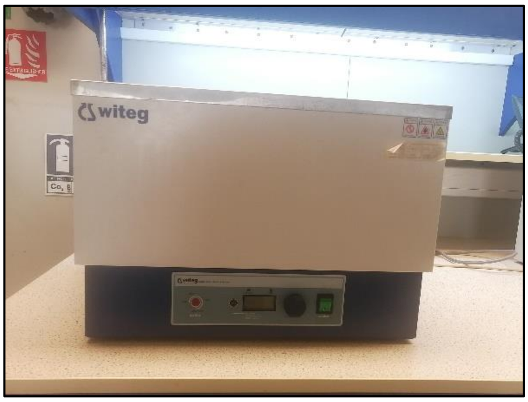
Appendix

Appendix A: Balance:

Appendix B: Water-bath:



Appendix C: Beakers & Glass Cylinder

Appendix D: Balance

Appendix E: Mixer

Figure III.11: Mixer. **[31]**

Appendix F: Pumping plot