

# Matrix Acidizing of Carbonate Formations: A Case Study

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## Abstract:

Formation damage is the impairment of permeability of rocks inside a petroleum reservoir occurs, during drilling, production, workover, stimulation and enhanced oil recovery operations, by various mechanisms such as chemical, mechanical, biological and thermal mechanisms. Near wellbore formation damages have a great impact on productivity or injectivity of the damaged formation. Acidizing is a stimulation method to remove the effect of near wellbore damage through reacting with damaging materials or the formation rocks (carbonate or sandstone rocks) to restore or improve permeability around the wellbore. Acid can be injected into the damaged formation below the fracture gradient of the formation which is called matrix acidizing. Acidizing operations is not only for treating the damaged formation, but also could be used for cleaning wellbore, production tubing and perforations from deposited scales prior to the matrix or fracture acidizing. The main objective of this paper is to achieve a homogeneous removal of formation damage through the entire pay zone of one of the Iraqi oil fields in order to increase well productivity index. The most common acid used in matrix acidizing of carbonate rocks (limestone or dolomite rock) is Hydrochloric acid (HCl); however, organic acids are preferably consumed in deep and high temperature wells due to high cost and uncontrolled corrosion problems with (HCl) acid. Various types of additives are added to the acid such as corrosion inhibitors, clay stabilizer, iron control agents and suspending agents. During the injection, the acid will flow into the least resistant (higher permeability) intervals in the formation due to heterogeneity or non-uniform damage in the formation and this prevents the damaged or low permeable sections from being stimulated. For achieving uniform acid treatment and diverting acid to the damaged zone, acid can be diverted mechanically or chemically. Each diversion technique has right conditions limitations to be applied depending on the formation situation. The name of the field is not mentioned in this work due to the confidentiality of publication and the well is named as Koya. Koya well is being drilled and completed at the carbonate pay zone, then the entire perforation zone being acidized to improve productivity. It has been observed that the production rate increases to 75% of the oil production rate.

**Keywords —** Damage, Permeability, Skin, Stimulation, Acidizing, Carbonate.

## 1.1. Introduction

Petroleum reservoir is a geological structure formed from porous and permeable rocks where hydrocarbons (oil and gas) are stored within the pores. Permeability and porosity are the most important properties of the reservoir rocks which reflect the capacity and productivity of the reservoir. Permeability is the ability of the reservoir rocks to transmit fluids through the connections (pore throats) between the reservoir rocks pores (Allen and Roberts, 1993). Therefore, permeability or conductivity of the reservoir rock pore shows the productivity of the petroleum reservoir. Hence, formation damage can be defined as any flow restriction that results in the reduction of natural permeability around the wellbore within the petroleum reservoir (gas or oil reservoir) that causes

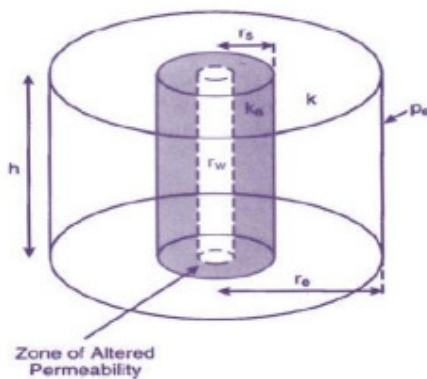
the reduction in hydrocarbon production (Bennion, 2002). Formation damage is the result of various mechanisms during drilling, cementing, production, work over and stimulation operations through the life of the oil well. These mechanisms, could be mechanical, chemical, biological and thermal, will result in natural or native reservoir permeability damage. One of the most common method of curing the damaged zone is matrix acidizing. Matrix acidizing means injecting a volume of an acid into the damaged formation at a pressure less than the formation fracture pressure. There are various types of acids such as mineral acids, organic acids and sulfamic acids, to be injected but each depends on mainly the formation rock properties, solubility, temperature, HSE and certainly the availabilities. In addition to the main acids, several additives are added to the treatment acid solution for

various objectives. The ratio or concentration of each additive in the acids should be practically determined based on tests on core and formation fluid samples.

When the acidizing treatment fluids flow into the formation, it has a high tendency to flow in to the least resistant intervals which have high permeability and less damage in the formation. This causes the failure of the stimulation because the interesting intervals, which are quite damaged or have very low permeability, are left behind without being treated or stimulated. Diversion techniques can overcome this problem and divert the treatment acid to the desired intervals or uniformly distribute the acid throughout the entire formation. In general, there are two types of diversion techniques: chemical diversion and mechanical diversion.

Selection of acid type and concentration is an essential stage in carbonate acidizing stimulation. Choosing the right concentration of acid should be based on laboratory tests (core flooding tests) on the formation core samples to investigate that which concentration of particular acid gives the ( Economides, Hill and Ehlig Economides, 1994)

permeability (Economides, Hill and Ehlig Economides, 1994)

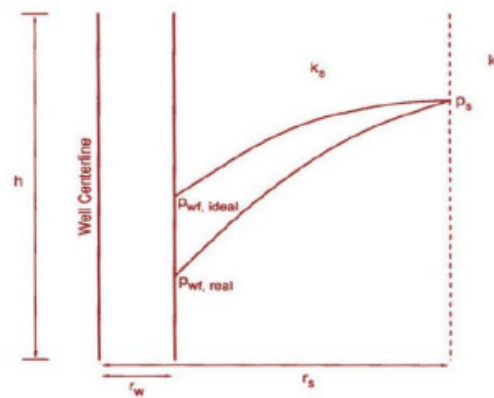


### 1.2. The influence of formation damage on productivity

Formation damage occurs within the reservoir in a short radius around the wellbore which causes reduction in permeability or relative permeability of hydrocarbons. This causes the reduction of bottom hole flowing pressure (P<sub>wf</sub>) and creates additional pressure drop as explained in figures (1) and (2).

Thus, as the damage has reduced the permeability from (k) to (k<sub>s</sub>), the bottom hole flowing pressure has been reduced from (P<sub>wf ideal</sub>) which is the bottom hole flowing pressure before the damage to (P<sub>wf real</sub>) after the damage. In 1949, Vaneverdingen and Hurst introduced a new term for measuring the formation damage around the well bore which is called Skin effect (S). They also introduced a relationship between the skin effect and the pressure drop across the skin zone as shown in equation (1).

$$\Delta P_s = \frac{q \mu}{2 \pi k h} S \dots \dots \dots \text{equ. 1}$$



In 1956, Hawkins invented another relation between the skin factor (S) and skin zone radius (r<sub>s</sub>) and the permeability of the damaged zone (k<sub>s</sub>) and undamaged zone (k). Figures (1) and (2) are helpful in developing this relationship. Hawkins established the relationship based on calculating the pressure drop around the wellbore for a radius of (r<sub>s</sub>) and considered the permeability of this zone as native permeability (k) of the reservoir before being damaged under a steady state radial flow condition as shown in equation (2).

$$P_s - P_{wf ideal} = \frac{q \mu}{2 \pi k h} \ln \left( \frac{r_s}{r_w} \right) \dots \dots \dots \text{equ. 2}$$

And the pressure drop across the same zone after the damage and reduction in permeability from (k) to (k<sub>s</sub>) will be:

Figure (2): Near wellbore zone, Ideal and real bottom hole flowing pressure (Economides, Hill and Ehlig Economides, 1994)

The difference between (P<sub>wf ideal</sub>) and (P<sub>wf real</sub>) is the pressure drop across the skin zone as shown in equation (4).

$$\Delta P_s = P_{wf ideal} - P_{wf real} \dots \dots \dots \text{equ. 4}$$

By rearranging the equations (2) and (3) and substitution of them with equation(1) in equation (4), the final form of Howkings relationship (Economides, Hill andEhlig-Economides, 1994) will be:

$$S = \left(\frac{k}{K_s} - 1\right) \ln\left(\frac{r_s}{r_w}\right) \dots \dots \dots \text{equ. 5}$$

The relationships in equations (1) and (5) show that the deeper formation damage(higher rs value) and the less permeability in the damaged zone (ks) means, the more skineffect (S) value and the more pressure drop (ΔPs) across the damaged zone. Hence,according to equation (4), the less (Pwf real)and less productivity. Skin effect (S) withnegative value indicates that the well has been stimulated. On the other hand, the positiveskin effect means that the well is damaged. Typically, the value of skin is raged between (-5) for a hydraulically stimulated well to infinity value for a completely damaged or pluggedwell (Allen and Roberts, 1993).

The effect of skin effect on the productivity of an oil or gas well can be explained betterwith the equation (6) which is introduced by Standing in 1970 (Sharma, 2007).

$$F = \frac{P_r - P_{wf} - \Delta P_s}{P_r - P_{wf}} \dots \dots \dots \text{equ. 6}$$

Where (F) is the flow efficiency of the wellbore. When there is no damage around the wellbore (S = 0), the pressure drop (ΔPs) aroundthe wellbore is zero and the flow efficiency is (1). The higher damage or skin effect (S)value causes higher pressure drop around the wellbore and eventually the less flowefficiency below (1) which means the less productivity of the well.

### 1.3. Formation damage mechanisms

Formation damage occurs due to variety mechanisms during drilling, production andcompletion operations. Basically, these mechanisms are categorized in to mechanical,chemical, biological and thermal formation damage.

#### 1.3.1. Mechanical formation damage

These mechanisms cause reduction of permeability by mechanically plugging of porethroats and this causes the formation damage. These mechanisms are:

- Fine migration
- Phase trapping
- Perforation damage
- Solid invasion

#### 1.3.2. Chemical formation damage

These refers to damages that are resulted from reasons that are related to theoccurrence of chemical reactions between the formation rocks and fluids with the chemicalsused in the oil well operations such as chemicals used in drilling, completion, stimulationand work over operations which can be subcategorized as:

- Swelling of clay minerals
- Clay de-flocculation
- Wettability alteration near the well bore
- Scale and organic deposits

#### 1.3.3. Biological formation damage

During drilling, completion, secondary recovery operations, bacteria (aerobic oranaerobic) might be introduced into the reservoir. Aerobic bacteria which needs oxygen, isonly problematic in water flooding operations which lasts for a long period. Sulfatereducing bacteria (SRB) which is and aerobic bacteria, causes formation damage bymetabolizing oil inside the porous media and produces polysaccharide polymers. Thepolymer product reduces permeability of the rocks and eventually productivity of theformation decrease (Bennion et al., 1995). Figure (3) shows the biofilm that has been made by bacterial cells under which the bacteria performs its activity.

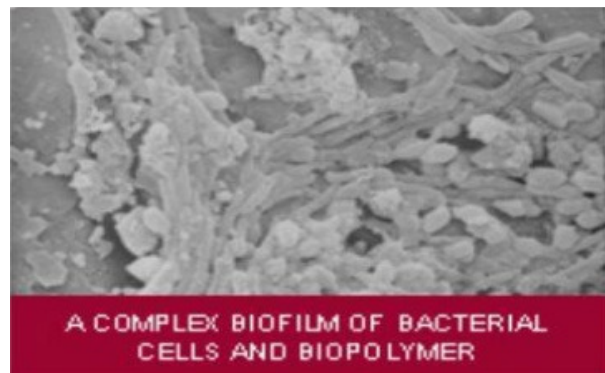


Figure (3): Bacterial formation damage (Microbial Formation Damage, 2012)

#### 1.3.4. Thermally induced formation damage

This class of formation damage only occurs in the heavy oil reservoirs during thethermal enhanced oil recovery operations such as hot water or steam injection and in-situcombustion. The heat transferred into or created in the reservoir causes damaging of the formation by:

- Mineral transformation
- Solubilization and precipitation

- or Wettability alteration

## 2. Acidizing Stimulation

Most wells, which are drilled in gas and oil reservoirs, need stimulation directly after the well is completed or during its production life for the purpose of improvement in the production capacity of oil or gas wells. Acidizing stimulation can only remove the effect of a number of the formation damage mechanisms which have been discussed. Generally, acidizing stimulation is the removal of near wellbore formation damage by dissolving the acid soluble plugging materials and the matrix formation rock. Acid may be used for cleaning the well bore and tubing or to improve the formation productivity and permeability such as matrix and fracture acidizing.

### 2.1. Types of acids used in matrix acidizing

#### 2.1.1. Mineral acids

Hydrochloric acid (HCl) is a strong acid which can be used in acidizing stimulation operations in both carbonate and sandstone formations. In carbonate formations usually a concentration of 15% by weight of HCl is used to stimulate limestone or dolomite rocks; however, higher concentrations (28% by weight) are desired in situations where deeper penetration of the rocks is considered. Hydrochloric acid also is used in acidizing stimulation of sandstone formations with the concentration of (5% to 15 % by weight) as a preflash before the injection of main treatment acid (HCl-HF mixture). This preflash dissolves the carbonate minerals in the sandstone formation to prevent the precipitation of insoluble calcium fluoride (CaF<sub>2</sub>) by the contact of Hydrofluoric acid (HF) with the carbonate minerals which caused permeability impairment near the well bore.

Despite the fact that, HCl has low cost and high dissolving power for carbonate minerals, it cannot be used at high temperature conditions such as in deep and high temperature wells where the acid reaction rate is very high which does not allow deep penetration of acid created wormholes; moreover, at these high temperature conditions, the corrosivity of the acid (HCl) cannot be controlled with inhibitors or the corrosion control is very expensive (Chang et al., 2008).

#### 2.1.2. Organic acids

Organic acids, which are weak acids and less corrosive compared to HCl acid, are rarely used except in high temperature situations or in operations that last for a long time and prolonged acid contact with the metal equipment is a big concern such as in perforation operations. Organic acids that are used in acidizing stimulation are:

- Acetic acid: the usage of 10% (by weight) concentration of acetic acid is common in acidizing stimulation because the acid – rock reaction products do not precipitate at this concentration. Acetic acid has a greater cost compared to HCl and formic acids (Williams, Gidley and Schechter, 1979).
- Formic acid: its properties are almost the same as acetic acid except that it has less ability to inhibit corrosion at high temperature conditions.

#### 2.1.3. Sulfamic acid (H<sub>3</sub>NSO<sub>3</sub>)

Sulfamic acid is an inorganic acid and it is usually in the form of powder or granular particles which allow its transportation easily to the well site and then it can be mixed with water to formulate the desired concentration. The usage of sulfamic in acidizing stimulation is problematic at temperatures higher than 180 °F because the acid will hydrolyze and form sulfuric acid. The generated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) reacts with the carbonate rocks or calcite scales (CaCO<sub>3</sub>) in the pores and results in the precipitation of insoluble Calcium sulfate (CaSO<sub>4</sub>) which reduces permeability (Allen and Roberts, 1993).

## 2.2. Acidizing stimulation additives

Various additives are added to the treatment acid solution for various objectives. The ratio or concentration of each additive in the acids should be practically determined based on tests on core and formation fluid samples. Common additives in acidizing stimulation operations are: corrosion inhibitors, surfactants, anti-sludge agents, suspending agents, mutual solvents, iron control additives and clay stabilizers.

## 2.3. Acid placement and diversion techniques

Due to heterogeneity of the damaged formations, permeability is not the same throughout the entire formation and even the degree of the damage varies within the same formation. When the acidizing treatment fluids flow into the formation, it has a high tendency to flow in to the least resistant intervals which have high permeability and less damage in the formation. This causes the failure of the stimulation because the interested intervals, which are quite damaged or have very low permeability, are left behind without being treated or stimulated.

Diversion techniques can overcome this problem and divert the treatment acid to the desired intervals or uniformly distribute the acid throughout the entire formation. In general, there are two types of diversion techniques: chemical diversion and mechanical diversion. Mechanical

diversion techniques are coiled tubing, ball sealers and bridge plug and packers, while chemical diversion includes the use of particulates, foam and viscous fluids in achieving the diversion. Mechanical diversion is more efficient and successful compared to chemical diversion; however, they are very expensive, and they need more time. Mechanical techniques only divert the acid in to the desired intervals inside the wellbore and cannot control the flow of the acid inside the matrix of the formation; therefore, they can be called external diversion techniques. Chemical diverters can achieve internal diversion of the acids (Chang et al., 2008).

### 3. Matrix Acidizing of Carbonate Formations

The aim of carbonate matrix acidizing is to remove the effect of near wellbore damage by dissolving the matrix of the rock and bypassing the damage by enlarging and connecting the pore spaces and creating new conductive channels. These conductive channels, which are referred as wormholes, penetrate the damaged zone up to few feet around the wellbore and bypass the permeability impairment. Acids used in carbonate matrix treatments are hydrochloric acid (HCl) or organic acids such as acetic acid (CH<sub>3</sub>COOH) or formic acid (HCOOH). These acids are only able to dissolve carbonate minerals; therefore, acid stimulation in carbonate rocks (limestone or dolomite) is principally achieved by dissolving the carbonate minerals in the rock matrix and fines that has been released from the rocks. Carbonate minerals that exist in carbonate rocks are calcite mineral (CaCO<sub>3</sub>) in limestone rock and dolomite mineral (CaMg(CO<sub>3</sub>)<sub>2</sub>).

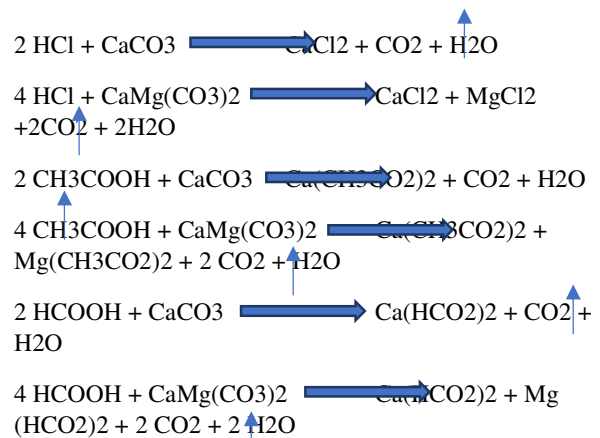
Selection of acid type and concentration is an essential stage in carbonate acidizing stimulation. Choosing the right concentration of acid should be based on laboratory tests (core flooding tests) on the formation core samples to investigate that which concentration of particular acid gives the optimum penetration or wormhole creation. In 1984, McLeod introduced a guide line for carbonate matrix acid stimulation as shown in table (1). 15% HCl is the most widely used in treatments of carbonate rocks; however, higher concentrations up to 28% can be used for achieving deeper penetration of the wormholes in deep near wellbore damage conditions.

Table (1): McLeod acid use guidelines (McLeod, 2007)

Situation	Weight Concentration
Perforating fluid	5% acetic acid
Damaged perforations	9% acetic acid, 10% formic acid, 15% HCl
Deep wellbore damage	15% HCl, 28% HCl, Emulsified HCl

#### 3.1. Carbonate rock composition and their reactions with acids:

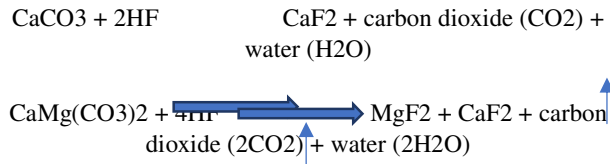
Limestone and dolomite are two types of sedimentary carbonate rocks that can be potential hydrocarbon reservoir rocks. They are called carbonate rocks due to having high percentage (above 50%) of carbonate minerals which have anionic carbonate (CO<sub>3</sub><sup>-2</sup>) group in their chemical composition. Limestone is mainly composed of calcite or calcium carbonate (CaCO<sub>3</sub>) mineral. Meanwhile, dolomite contains Magnesium ions as well. Reaction of common acids (organic acid or HCl) acid in carbonate matrix acidizing with carbonate minerals in carbonate rocks results in the production of carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and salts that are soluble in water and the spent acid such as magnesium chloride (MgCl<sub>2</sub>), calcium chloride (CaCl<sub>2</sub>), calcium acetate (Ca(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>), magnesium acetate (Mg(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>), calcium formate (Ca(HCO<sub>2</sub>)<sub>2</sub>) and magnesium formate (Mg(HCO<sub>2</sub>)<sub>2</sub>) as shown in the following reaction equations (Kalfayan, 2008):



Carbonate rocks may not be pure and siliceous minerals can co-exist with the carbonate minerals in the rock. These siliceous minerals could be quartz or clay minerals that exist in sandstone, shale or chert rocks. In the presence of a considerable percentage of siliceous minerals (less than 50%), the carbonate rock is named as sandy, cherty or shaly carbonate (dolomite or limestone) rock (Williams, Gidley and Schechter, 1979, P.12). Acids which are used in carbonate acidizing cannot dissolve siliceous minerals (minerals that contain silicon in their chemical composition) such as clay minerals (Kaolinite, Illite, Smectite and Chlorite), Quartz, Mica and Feldspar.

The percentage of impurities and carbonate minerals in the carbonate rock should be known which affects the design of the acid volume and acid penetration depth. (Allen and Roberts, 1993, p.7-19) explains that, the use of hydrofluoric acid (HF), which is specialized for sandstone acidizing stimulation and powerful in dissolving siliceous minerals, in carbonate formations should be shunned because (HF) reacts with carbonate minerals and produce

insoluble reaction products (magnesium fluoride (MgF<sub>2</sub>) /or calcium fluoride(CaF<sub>2</sub>)) inside the rock pores which causes the damage of the formation and permeability impairment rather than stimulation as shown below:



**3.2. Estimation of the required acid volume for carbonate matrix acidizing:**

(Economides, Hill and Ehlig-Economides, 1994) has presented two models for estimating the required acid volume for matrix treatment of carbonate formations which are Daccord’s model and volumetric model. The later will be discussed in this paper. Volumetric model assumes that in carbonate matrix acidizing, a constant fraction of the carbonate rock will be dissolved by the acid. Laboratory tests on core samples should be carried out to attain this fraction. The dissolved fraction of the reservoir rock in the entire formation will be the same as the dissolved fraction in the core samples. Equation (7), which is an empirical equation, is used in volumetric model for calculating the required acid volume:

$$\frac{V}{h} = \frac{\pi \phi \eta (r_{wh}^2 - r_w^2)}{N_{Ac}} \dots \dots \dots \text{equ. 7}$$

- Where:
- $\frac{V}{h}$ : The required acid volume per unit thickness of the formation in (ft<sup>3</sup>/ft).
  - $\phi$ : Formation porosity.
  - $\eta$ : Fraction of the rock that dissolved by the acid.
  - $r_{wh}$ : Penetrated radius by the wormholes in (ft).
  - $r_w$ : Wellbore radius in (ft).
  - $N_{Ac}$ : Acid capacity number, dimensionless

The fraction of the rock ( $\eta$ ) which is dissolved by the acid in the core sample can also be determined by using equation (8):

$$\eta = N_{Ac} PV_{bt} \dots \dots \dots \text{equ. 8}$$

( $PV_{bt}$ ) is the number of pore volumes that has been filled or injected with acid when the wormholes breakthrough at the core sample end. The ( $PV_{bt}$ ) can be found in laboratory experiments on the core samples by using neutron radiography which film the enlarged pores and created wormholes in the cores.

**3.3. Acid injection rate**

Maximum allowable acid injection rate without creating fracture in the formation can be found with equation (9). It is recommended to keep the acid injection rate at 10% lower than the maximum allowable injection rate as a safety margin to avoid breaking the formation.

$$(q_{iac})_{max} = \frac{4.917 \times 10^{-6} k_{av} h_n (g_f D - P_R)}{\mu_{ac} \ln(r_e/r_w)} \dots \dots \dots \text{equ. 9}$$

- Where:
- $(q_{iac})_{max}$ : Maximum allowable acid injection rate (bbl/min)
  - $k_{av}$ : Average formation permeability (md)
  - $h_n$ : Formation thickness (ft)
  - $g_f$ : Formation fracture gradient (psi/ft)
  - $D$ : Formation depth (ft)
  - $P_R$ : Reservoir pressure (psi)
  - $\mu_{ac}$ : Acid viscosity (cp)
  - $r_e$ : Reservoir drainage radius (ft)
  - $r_w$ : Wellbore radius (ft)

**3.4. Maximum allowable surface injection pressure**

Acid injection pressure should not exceed the maximum allowable limit, which can be found by using equation (10), to avoid the breakage of the formation:

$$P_{max} = [g_f - 0.052(\rho_{acid})] D \dots \dots \dots \text{equ. 10}$$

- Where:
- $P_{max}$ : Maximum allowable acid injection pressure at surface (psi)
  - $g_f$ : Formation fracture gradient (psi/ft)
  - $\rho_{acid}$ : Density of the acid (ppg)
  - $D$ : Formation depth (ft.)

**4. Case Study**

A “Koya” well is being drilled and completed in one of the filed at north of Iraq, the name of the field is not mentioned in this work due to the confidentiality of publication. The perforation interval was 20 m from 1774 m to 1794 m in carbonate formation. It was observed that the pressure difference between the Pws and Pwf around 300 psi which is too high, and the well was producing 3150 bbls/day. Therefore, it has been decided to stimulate the well through acidizing the whole perforation zone, the acidizing procedure information are shown in tables below.

Main Acid			5,544 gals 132 bbls			
Mixing Order	20% HCl (Main Treatment)		Concentration for		Concentration for	
	Additive	Description	1,000	gal	132	bbls
1	Water	Fresh Water	383	gal	2,123	gal
2	S101	Corrosion Inhibitor	6	gal	33	gal
3	S243	Non Emulsifying Agent	2	gal	11	gal
4	S222	Anti-Sludge Agent	2	gal	11	gal
5	S261	Iron Sequestering Agent	10	gal	55	gal
6	S281	Surfactant	4	gal	22	gal
7	HCl	32% HCl	593	gal	3,288	gal

Table (2): Main fluid 20% HCl (Koya well)

Table (3): Diesel displacement (Koya well)

Diesel			2,730 gals 65 bbls			
Mixing Order	Diesel		Concentration for		Concentration for	
	Additive	Description	1,000	gal	65	bbls
1	Diesel	Diesel	1000	gal	2,730	gal

#### 4.1. Results and discussions

The well being acidized through injecting 132 bbls of 20% HCl at a pressure of 2800 psi with a rate of 8 bbl/min then being displaced with 65 bbls of diesel. It has been observed the pressure difference between the Pws and Pwf decreased from 300 psi to 25 psi and the production rate being increased from 3150 bbls/day to around 5500 bbls/day.

#### 5. Conclusion

- Formation damages could be occurred at various operations such as drilling, completion, production and EOR.
- Formation damage has a significant affect on the production rate since reduce the permeability of the pay zones.
- Formation Damage Mechanisms are classified into Four categories; mechanical, chemical, biological and thermal.
- Stimulation is the remedial of the formation damage and classifies into matrix acidizing and fracturing.
- Various types of acids are used in matrix acidizing and each is suitable for specific type rocks and conditions.
- In addition to the main acid fluid, there are several chemical to be added to the acid solution called additives.
- The acids could reach the target interval through various diversion techniques such as chemical and mechanical diversions.

- The main acid used in carbonate formation is HCl with different concentrations
- The acidizing operation should be designed regarding the type of acid, the concentration of acid, the volume of acid, injecting rate and injecting pressure.
- In the mentioned case study, result showed that the production rate increases to approximately 75% of the oil production rate.

#### 6. Recommendations

- Doing both compatibility test and core flooding test in order to decide on the type of acid and its concentration.
- Determining the formation fracture gradient in order to avoid fracturing while matrix acidizing.
- The ability or advantages of hydraulic fracturing over the matrix acidizing for certain formation.

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