MATRIX ACIDIZATION JOB DESIGN

A Project Report

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Dr. Pushpa Sharma

(Professor, Petroleum and Earth Sciences UPES)

UNIVERISTY OF PETROLEUM & ENERGY STUDIES

DEHRADUN

DECLARATION BY THE SCHOLAR

We hereby declare that this submission is our own work and that, to the best of our knowledge and belief, it contains no material previously published or written by anot-her person nor material which has been accepted for the award of any other Degree or Diploma of the University or other institute of higher learning, except where due acknowledgement has been made in the text.

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CERTIFICATE

This is to certify that the thesis titled “**Acidization Job Design**” submitted by **HITESH MITTAL** (R870212017), **SATYAPRAKASH** (R870212032), **SAURABH KUMAR GUPTA** (R870212033), to the **UNIVERSITY OF PETROLEUM AND ENERGY STUDIES**, for the award of the degree of BACHELOR OF TECHNOLOGY in Applied Petroleum Engineering is a bonafide record of project work carried out by them under my supervision and guidance. This content of the thesis, in full or parts have not been submitted to any other institute or University for the award of any other degree.

Dr. Pushpa Sharma

Professor

Date: ……………………….

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ABSTRACT

To maintain pressure control during drilling, completion or work over of a well the operations are usually done at overbalanced condition, these overbalanced condition results in influx of fluids and solids from wellbore into formation. The net effect of invading fluid interaction with formation is generally detrimental. The result is near wellbore formation damage causing additional pressure drop in the vicinity of wellbore and a reduction in well productivity.

Acidizing is a matrix treatment that is carried out at a pressure lower than the formation breakdown pressure whereby acid is injected into the formation to improve well productivity. The type of acid to be used depends on the type of formation.

Well stimulation techniques are applied on regular basis to enhance productivity and maximize recovery in oil and gas wells. Among these techniques, matrix acidizing is probably the most widely performed job because of its low cost compared to hydraulic fracturing, and suitability to both generate extra production capacity and to restore original productivity in damaged wells. The principal involves injecting an acid solution into the formation at a pressure below the fracture pressure with the primary objective of removing damage near the wellbore, hence restoring the natural permeability and improving well productivity. Reservoir heterogeneity plays a significant role in the selection and design of acidizing treatment. The success of acidizing treatment is strongly related to dissolution pattern of matrix. The standard acid treatments are HCl mixtures (to dissolve carbonate minerals) and HCl-HF formulations to attack plugging minerals, mainly silicates (clays and feldspar).

NOMENCLATURE

k - Permeability of the formation, milli Darcy

k_s - Permeability of the invaded zone, m

q - Flow rate of fluid, m^3/s

p - Pressure of the reservoir fluid, psi

p_s - Pressure due to skin, psi

P_{wf} - Flowing bottomhole pressure, psi

t - Time in seconds

$\varnothing$ - Porosity of the formation

ρ - Density of the fluid, kg/m^3

μ - Viscosity of the fluid, cP

ν - Poisson's ratio

FG - Fracture gradient of the formation

i - Injection rate, m^3/s

V - Volume of the acid, m3

S - Skin factor

r_e - Drainage radius, m

r_w - Radius of the wellbore, m

r_s - Radius of the invaded zone, m

$D_a^{(R,F)}$ - Radial Damkohler number for fast reacting minerals

$D_a^{(R,S)}$ - Radial Damkohler number for slow reacting minerals

$A_c^{(F)}$ - Acid capacity number for fast reacting minerals

$A_c^{(F)}$ - Acid capacity number for slow reacting minerals

$\varepsilon_f^{(R)}$ - Reaction front distance, m

δ - Reaction zone width, m

ψ - Acid concentration ratio on the upstream side

h - Thickness of the formation, m

r_w - Effective radius in the presence of skin

$c_{HF}°$ - Acid concentration in Kg.mole/m^3

β_F - Moles of mineral per mole of HF

S_2 - New skin factor after the treatment

HF - Hydrofluoric acid

HCl - Hydrochloric acid

IARF - Infinite acting radial flow

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Chapter 1 Introduction

Well stimulation techniques are applied on a regular basis to enhance productivity and maximize recovery in oil and gas wells. Among these techniques, matrix acidizing is probably the most widely performed job because of its relative low cost, compared to hydraulic fracturing, and suitability to both generate extra production capacity and to restore original productivity in damaged wells. The acidizing process leads to increased economic reserves, improving the ultimate recovery in both sandstone and carbonate reservoir.

Matrix acidizing consists of injecting an acid solution in to the formation, at a pressure below the fracture pressure to dissolve some of the minerals present in the rock with primary objective of removing damage near the wellbore, hence restoring the natural permeability and greatly improving well productivity . reservoir heterogeneity plays significant role in the success of acidizing treatment because of its influence on damage removal mechanism ,and strongly related to dissolution pattern of matrix the standard acid treatment are HCL mixture to dissolve carbonate minerals and HCL-HF formulation to attack those plugging minerals , mainly silicates (clays and feldspars).

Well testing plays significant role for successful execution of acidization treatment it provides necessary information required for designing of acidization job like skin factor , Extent of radical damage, average reservoir permeability etc. data obtained during well testing operation is studied with the help of testing software (SAPPHIRE). With the help of software using semilog plot skin, average permeability can be determined. It also has importance in post acid job evaluation. Effectiveness of acidization job is gauged in terms of increment in productivity index. Ratio of productivity index requires skin factor which has to be calculated real time. Real time monitoring of skin facilitate any modification during execution of job as well as determine productivity index ratio.

Additives like corrosion inhibitor, surfactants, organic solvents etc. are also added in acid mixture to make acidization efficient. Additives are added to prevent perpetration of any insoluble reaction products. In case of multilayer reservoir, acidization is performed with proper acid placement techniques and diverting agents (Ball sealers, Straddle Packer, Polymers).

Literature Review

Acids

Acids are used for matrix treatment, as fracturing fluids, for scale removal and to clean up gravel packs. To be able to select the appropriate acid for the required treatment it is necessary to understand the chemical reaction of different acid with reservoir minerals.

Acid systems

Acid system in current use can be classified as mineral acids, dilute acids powdered organic acids hybrid acids or retarded acid. The most common members of each category is listed in the underlying table-

Category	example of acids used in well treatment
Mineral acid	hydrochloric acid
	hydrochloric acid- hydrofluoric acid
Organic acids	formic acid
	acetic acid
Powdered acid	sulfamic acid
	chloroacetic acid
Mixed acid	acetic - hydrochloric acid
	formic - hydrochloric acid
	formic - hydrofluoric acid
Retarded acid	gelled acids
	Emulsified acids

Table 1.1 Categories of acids and example systems, courtesy: Schechter

All of these acids with the exception of HCl-HF and HCOOH-HF acid mixture are used to treat carbonate formations. It is with this exception, it is necessary to include hydrofluoric acid in the treatment of sandstone formation.

Stoichiometry of acid carbonates reactions:

Stoichiometry refers to the proportion of various reactants that enters into the reaction. This proportion can be easily identified in the reaction of calcium carbonate or dolomite with HCl, in addition to HCl other organic acids can also be used to treat carbonate formation. The reaction are-

$$\underset{\text{(calcite)}}{2HCl + CaCO_3} \rightleftharpoons CaCl_2 + H_2O + CO_2 \, .$$

$$4HCl + \underset{\text{(dolomite)}}{CaMg(CO_3)_2} \rightleftharpoons MgCl_2 + CaCl_2 + 2H_2O + 2CO_2 \, .$$

Dissolving power (β):

The gravimetric dissolving power is defined as mass of rock dissolved per unit mass of acid. Given the reaction stoichiometry, dissolving power can be easily calculated as following -

$$\beta = \left[\frac{1 \text{ mole } CaCO_3}{2 \text{ moles } HCl}\right] \left[\frac{\text{molecular weight } CaCO_3}{\text{molecular weight } HCl}\right] \left[\frac{\text{mass } HCl}{\text{mass acid solution}}\right] \quad \text{… (1.1)}$$

An even more useful concept is the volumetric dissolving power (X), which is defined as the volume of rock dissolved per unit volume of acid reacted. The volumetric dissolving power is related to gravimetric dissolving power simply by the equation-

$$X = \frac{\beta \ Pacid}{Paco_3} \quad \text{……………………………… (1.2)}$$

The dissolving power of various acids is listed below-

Formation	Acid	β_{100}	X 5%	 10%	 15%	 30%
Limestone:	Hydrochloric (HCl)	1.37	0.026	0.053	0.082	0.175
$CaCO_3$	Formic (HCOOH)	1.09	0.020	0.041	0.062	0.129
$\rho_{CaCO_3} = 2.71$ g/cm^3	Acetic (CH_3COOH)	0.83	0.016	0.031	0.047	0.096
Dolomite:	Hydrochloric	1.27	0.023	0.046	0.071	0.152
$CaMg(CO_3)_2$	Formic	1.00	0.018	0.036	0.054	0.112
$\rho_{CaMg(CO_3)_2} = 2.87$ g/cm^3	Acetic	0.77	0.014	0.027	0.041	0.083

Data for organic acids have not been corrected for equilibrium

Table 1.2 Dissolving power of various acids

When an acid reaction reaches equilibrium the formation material by the acid stopes, even though the acid molecules may still be present. Equilibrium is attained when the chemical activity of the reaction products balances the chemical activity of the reactants.

Consider a general reaction

$$A + B \rightleftharpoons C + D$$

The equilibrium constant for this reaction is defined as

$$K = \frac{a_C a_D}{a_A a_B} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.3)}$$

The quantity a_i the activity component i. these activities are thermodynamic potentials. The activity of the component increases with its concentration in the solution but they do not exhibit a linear relationship.

Reaction equilibrium:

Under reservoir condition organic acids does not react to completion with either limestone or dolomite because of the limitation imposed on the chemical equilibrium. Equilibrium occurs in reservoir because CO_2 is held in solution by reservoir pressure and is not allowed to escape from the solution. At low pressure however CO_2 can escape and acid reaction reaches to equilibrium. It has been that equilibrium state can be predicted approximately by the empirical equation-

$$1.6 \times 10^4 K_D = \frac{c_{CaA_2} c_{CO_2}}{c_{HA}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.4)}$$

Here c_i is concentration of component i in g moles /1000 gm of H_2O. Once the extent of reaction is determined the correct dissolving power can be obtained.

Stoichiometry of acid - sandstone reactions:

For treating sandstone formation normally a mixture of HF-HCl is employed. An acid mixture is employed here because HF reacts with clay minerals and feldspars that may be restricting the permeability near the wellbore. Chemical reaction between HF and silica or calcite is comparatively simple but HF reaction with aluminosilicates such as clays or feldspar is quite complex.

Equation describing the reaction of HF with silicates (SiO_2) is as follows:

$$SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \rightleftharpoons H_2SiF_6$$

The reaction products are highly soluble in water. In the presence of large excess of HF the reaction product is H_2SiF_6 whereas if SiO_2 is in excess the reaction product is primarily SiF_4, depending on which product dominates the dissolving power may vary.

HF reacts with $CaCO_3$ as follows –

$$CaCO_3 + 2HF \rightleftharpoons CaF_2 + H_2O + CO_2$$

The reaction product of CaF_2 is not soluble in water and thus this may lead to permeability loss, for the same reason a perflush of HCl is employed for treating sandstone formation.

The reaction of HF and HCl mixture with aluminosilicates such as feldspars and clays is as follows-

$$NaAlSi_3O_8 + 14HF + 2H^+ \rightleftharpoons Na^+ + AlF_2^+ + 3SiF_4 + 8H_2O$$

The reaction products AlF_2^+ and SiF_4 will be predominate once formed for a limited range of solid to acid ratios.

Equilibrium in acid –sandstone reactions:

Solution of HF and HCl mixture contain many species including H^+, F^-, HF_2^-, HF, which of these will be present in dominant concentration depends on the concentration of HF and HCl in the solution.

Association of HF is represented as:

$$HF \rightleftharpoons H^+ + F^-$$

$$2HF \rightleftharpoons HF_2^- + H^+$$

And the equilibrium constant is defined as-

$$K_D = \frac{[H^+][F^-]}{[HF]} \qquad \text{……………………} \ (1.5)$$

And

$$K_D = \frac{[H^+][HF_2^-]}{[HF]^2} \qquad \text{……………………} \ (1.6)$$

For the respective association.

We note at in the presence of an excess amount of clay, the aluminium fluoride compounds are more stable than the silicon fluorides and the initial reaction product H_2SiF_6 begins to loss fluorine to more stable aluminium compound, as the reaction proceeds ultimately $Si(OH)_4$ is formed and these precipitants may be damaging to the rock permeability and thus should be minimized .

Acid treatment

In this section matrix acidizing of both sandstone and carbonates is discussed . The treatment is described as the injection of acid in to the formation porosity at a pressure lower than the fracture pressure of the formation. Matrix acidizing is most useful in treating highly permeable but damaged zones, if carried out successfully then matrix acidizing leads to increase in production of oil without subsequently increasing water and gas production as the case may be.

Acid is also used in washing the perforation removing scale deposits on tubular goods by spotting the acid in the wellbore it to react without agitation.

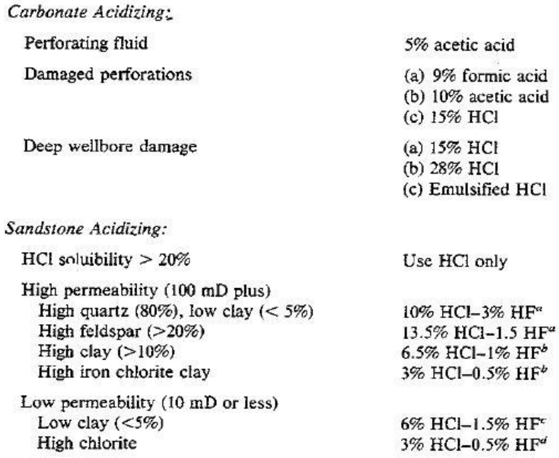
Acid are also used for acid fracturing and the following purpose-

- As a spearhead when fracturing to clean out perforation.
- To break acid sensitive gels used in fracture treatment.
- A perflush before squeeze cementing.
- Acidizing a completed gravel pack when the permeability of the gravel pack is impaired.

Types of acid

In matrix acidizing various acids may be appropriate depending on the particular situation. Any choice of the treatment acid should be derived from consideration of the specific problem with utilization of all the available information. Matrix acidizing involves the concentration of the acid, the volume of the acid to be injected at an appropriate injection rate. Matrix acidizing of sandstone also includes an perflush and an afterflush. The appropriate formulation depends on the mineralogy and the petrology of the formation rock.

Following table has been prepared by McLeod as a guideline for the acid selection.



Carbonate Acidizing:	
Perforating fluid	5% acetic acid
Damaged perforations	(a) 9% formic acid (b) 10% acetic acid (c) 15% HCl
Deep wellbore damage	(a) 15% HCl (b) 28% HCl (c) Emulsified HCl
Sandstone Acidizing:	
HCl soluibility > 20%	Use HCl only
High permeability (100 mD plus)	
High quartz (80%), low clay (< 5%)	10% HCl–3% HF[a]
High feldspar (>20%)	13.5% HCl–1.5 HF[a]
High clay (>10%)	6.5% HCl–1% HF[b]
High iron chlorite clay	3% HCl–0.5% HF[b]
Low permeability (10 mD or less)	
Low clay (<5%)	6% HCl–1.5% HF[c]
High chlorite	3% HCl–0.5% HF[d]

Table 1.3 Guidelines for acid selection, courtesy: Schechter

Acid is injected into the formation by pumping in from the surface containers and through tubing, allthe materials that come in contact with the acid should be thouroughly cleaned otherwise the acid insoluble solids deposits (oxide scale, pipe dope, paraffin, asphaltene) will all be carried to the formation creating further damage, if he reservoir pressure is too low to lift the acid back a foamed acid should be used, proper spotting of acid is also crucial. To be successful it is necessary that acid must be directed, directly to the damaged zone.

Theoretical productivity improvement

A matrix acidizing treatment is effective primarily in the damaged zone near the wellbore. In this system a zone of reduced permeability (K_s) extends from the well bore radius (r_w) to a radius of r_s beyond this the formation has a constant permeability of k to the drainage radius r_e.

$$\frac{J_d}{J_0} = \frac{(k_s/k)\ln(r_e/r_w)}{\ln(r_s/r_w) + (k_s/k)\ln(r_e/r_s)} \quad \text{……………………………………………………………………………… (1.7)}$$

Here J_o is the productivity index of the undamaged formation and J_d of the same damaged formation.

Maximum injection rate

The well pressure P_{wf} to inject the fluid in to the formation having a drainage radius of r_e and the reservoir pressure P_R is given by-

$$p_{wf} - p_R = \frac{i\mu}{2\pi kh}\left[\ln\left(\frac{r_e}{r'_w}\right) - \frac{3}{4}\right] \quad \text{…………………………………………………………………………… (1.8)}$$

Here r'_w is the effective radius in the pressure of skin, given by

$$r'_w = r_w \exp(-S) \quad \text{…………………………………………………………………………………………………… (1.9)}$$

The maximum injection rate i_{max} is found when

P_{wf} = (FG)*D ………. (1.10)

FG here is the fracture gradient and D is the formation depth.

Acid reaction with reservoir minerals

Acid reaction with reservoir minerals are heterogeneous reaction since they occurs at the interface between solid and liquid rather than in the bulk phase. The observed overall reaction is represented by disappearance of the acid from the solution. The disappearance of acid is composed of various mechanism occurring in the series. It is important to understand all of these steps since one of the steps is the slowest step and the rate at which this slowest step progress determines the overall rate of reaction upon changing the thermal and chemical environment the rate controlling steps also changes.

The observed reaction rate is the time rate of change of concentration of one component in the bulk liquid phase. The rate of acid transfer to the reactive mineral surface by diffusion, forced conversion, free conversion or fluid loss is the first step. The second step is the reaction rate determined by the kinetics of the surface reaction.

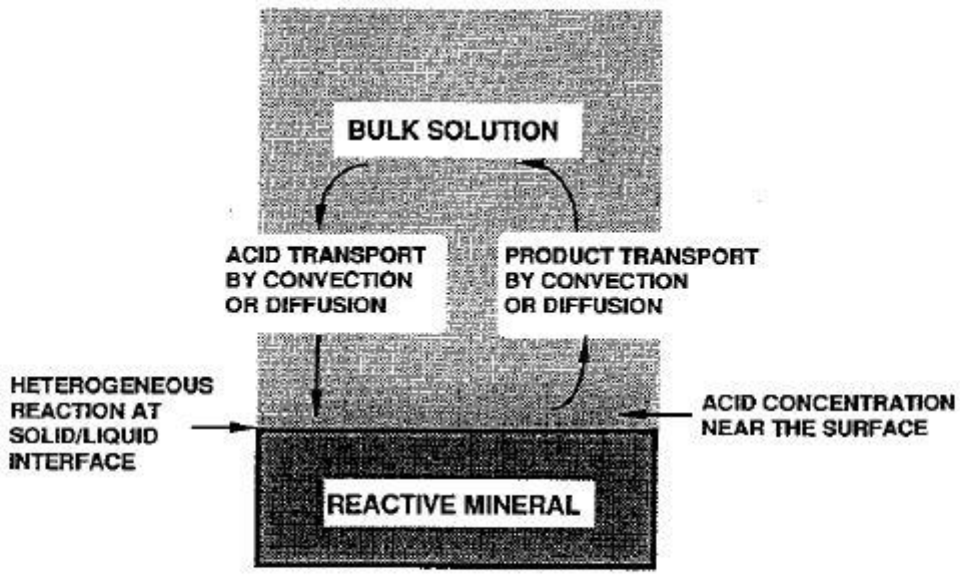


Figure 1.1 schematic diagram of the system in which acid reaction occur, courtesy: Schechter

Rate of surface reaction

The rate of the heterogeneous reaction is a function of the chemical composition of the liquid phase evaluated near the surface, such concentration are called as surface concentration. And further these surface concentrations can be related to the bulk phase concentration.

The rate of heterogeneous reaction is expressed as an amount of chemical species produced per unit of surface per unit of time. The surface area refer to mineral solution wetted area

Consider a heterogeneous reaction of HCl with calcium carbonate-

$$2H^{+} + CaCO_3 \underset{E_R}{\overset{E_f}{\rightleftharpoons}} CO_2 + Ca^{++} + H_2O \, .$$

Or in symbolic terms-

$$2A + B \underset{E_R}{\overset{E_f}{\rightleftharpoons}} C + D + E$$

For this reaction a general rate expression is –

$$-r_A = E_f c_A^\alpha c_B^\beta - E_R c_C^\gamma c_D^\delta c_E^\epsilon \tag{1.11}$$

Here C_i is the surface concentration of component I, E_b and E_f are the forward and backward reaction are constants.

Strong acid such as highly dissociated HCl when used to treat formation, the reaction essentially goes to completion and thus the backward rate will be negligible in most application of strong acids, and thus the reaction rate expression reduces to

$$-r_A = E_f c_A^\alpha \tag{1.12}$$

Here α is a constant and is known as the order of reaction.

Weak acids such as formic, acetic, propionic and other organic acids dissociate slightly and thus the backward reaction rate can't be neglected in this case. An acid HA dissociates according to the relation

$$\mathbf{HA \rightleftharpoons H^+ + A^-}$$

With equilibrium described by dissociation constant (K_d) defined as

$$K_d = \frac{c_H c_A}{c_{HA}} = \frac{c_{H^+}^2}{c_{HA}} \tag{1.13}$$

And thus the rate expression is given as

$$-r_A = E_f c_H^\alpha - E_R c_{CO_2}^{\alpha/2} c_{Ca}^{\alpha/2} \tag{1.14}$$

Feldspar-hydrofluoric reactions:

The silicates primarily feldspars, clays with the exception of chlorite does not react with HCl. These minerals do however reacts with HF. Feldspar may be divided into two major groups: the orthoclase group and the plagioclase group. The dissolution kinetics of feldspar in HF-HCl mixture are found to obey the following rate law-

$$+r_{\mathrm{feldspar}} = E_f[1 + K(c_{HCl})^\beta](c_{HF})^\alpha \tag{1.15}$$

For **potassium feldspar (orthoclase)** the kinetic parameters have the following values

$\beta = 0.4$; **$\alpha = 1.2$**

And the rate constant obeys the following relation-

$$E_f = 1.27 \times 10^{-1} \exp\left(-\frac{4680}{T}\right) \quad \text{and,} \quad K = 5.66 \times 10^{-2} \exp\left(\frac{956}{T}\right) \qquad \text{...... (1.16)}$$

For **sodium feldspar (albite)** the kinetic parameters representing the kg moles of albite per m^2 per sec have the following values-

$\beta = 1.0$; **$\alpha = 1.0$ and**

$$E_f = 9.50 \times 10^{-3} \exp\left(-\frac{3930}{T}\right); \quad K = 6.24 \times 10^{-2} \exp\left(\frac{554}{T}\right) \qquad \text{.......... (1.17)}$$

These rate expression are expressed in terms of orthoclase or albite which enters the solution.

Quartz - Hydrofluoric acid reactions-

The reaction rate of quartz with HF has been investigated by Bergman at 298 Kelvin

$$r_{HF} = -E_f c_{HF}. \qquad \text{............ (1.18)}$$

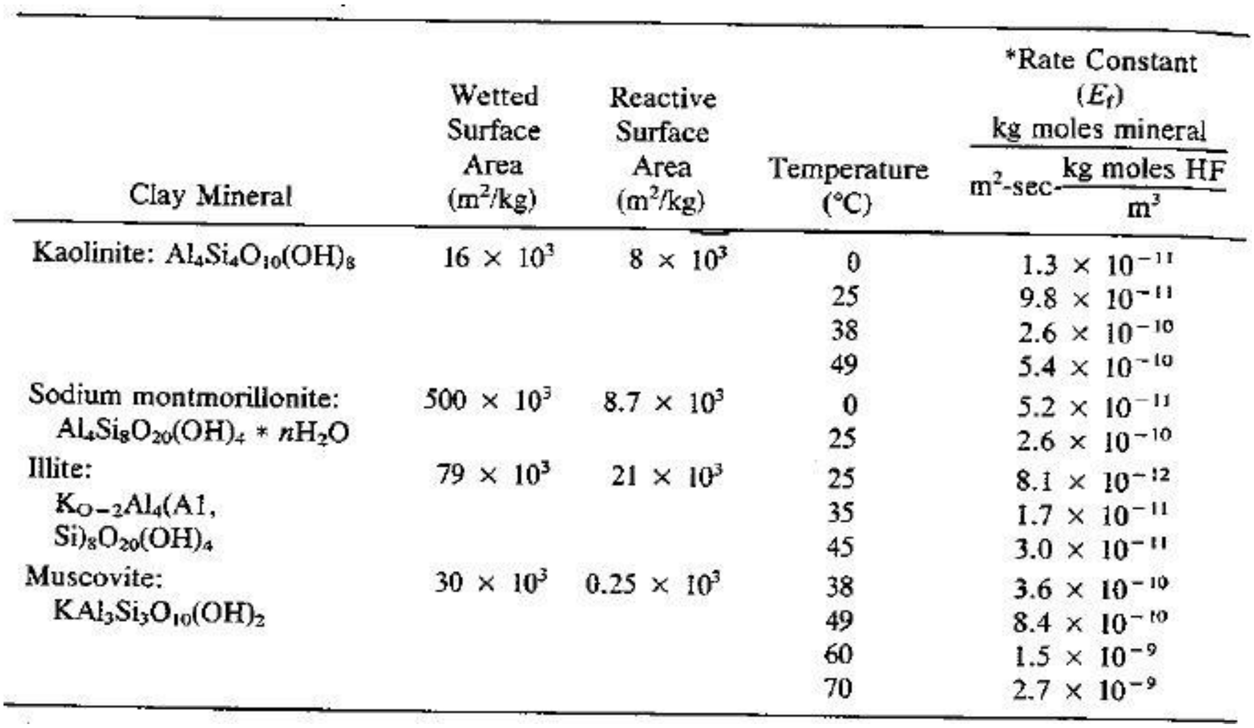
Clay - hydrofluroic reactios-

The reaction of clay minerals with HF has been investigated by Kline and Fogler. The cavity clay reactivity was found not to be proportional to the surface areas of the clay in contact with the acid solution, the surprising difference in the reaction rate per unit area can be understood in terms of the respective crystalline structure of clays. Kalonite is two layer clay with alumina and silica sheet bound together whereas montmorillonite is a three layer cay in which alumina sheet is sandwiched between silica sheets. The alumina sheet is much more reactive then silica and thus for the same reason kalolinite tends to be attacked faster than montmorillonite. Acid reacts with alumina sheet producing holes that expose other layers to the acid, whereas montmorillonite on the other hand tend to dissolves from the edges first; the actual reactive area of the montmorillonite is thus only a small fraction of the exposed area and the kalonite reacts much faster.

The rate constants can also be expressed in terms of the aluminium produced. The rate of dissolution of clay is given by-

$$r_{clay} = -E_f c_{HF}. \qquad \text{............ (1.19)}$$

E_f is the forward rate constant obtained from the underlying table for different clays:



Clay Mineral	Wetted Surface Area (m^2/kg)	Reactive Surface Area (m^2/kg)	Temperature (°C)	*Rate Constant (E_f) $\frac{\text{kg moles mineral}}{m^2\text{-sec-}\frac{\text{kg moles HF}}{m^3}}$
Kaolinite: $Al_4Si_4O_{10}(OH)_8$	16×10^3	8×10^3	0	1.3×10^{-11}
			25	9.8×10^{-11}
			38	2.6×10^{-10}
			49	5.4×10^{-10}
Sodium montmorillonite: $Al_4Si_8O_{20}(OH)_4 * nH_2O$	500×10^3	8.7×10^3	0	5.2×10^{-11}
			25	2.6×10^{-10}
Illite: $K_{O-2}Al_4(Al, Si)_8O_{20}(OH)_4$	79×10^3	21×10^3	25	8.1×10^{-12}
			35	1.7×10^{-11}
			45	3.0×10^{-11}
Muscovite: $KAl_3Si_3O_{10}(OH)_2$	30×10^3	0.25×10^3	38	3.6×10^{-10}
			49	8.4×10^{-10}
			60	1.5×10^{-9}
			70	2.7×10^{-9}

Table 1.4 Forward rate constants for different clays, courtesy: Schechter

Chapter 2 Formation damage: Origin and Removal

Origin of formation damage

It describes the origin of formation damage and review all the operation on the well, from drilling to cementing, completion, gravel packing, production, stimulation, and injection for enhanced oil recovery. All are potential source of damages.

Drilling damage

Drilling mud solid invasions

Such a damaging process is limited to the first few inches around the wellbore (an average value of 3 inch (7.5 cm) is commonly used), but the resultant permeability reduction can be as high as 90 %.

Invasion of formation rock by drilling fluid solids is favored by:

- Large pore size of the formation rock.
- Presence of fissures and natural fractures in the reservoir.
- Small particle size of the solid components of the drilling fluid (weighting agents and lost-circulation preventers whose initial particle are usually cores and can be fragmented by the drilling bit.
- Low drilling rate resulting in mud cake destruction (mud loss increase) and long mud-to-formation contact time.
- High drilling fluid circulation rate (mud cake erosion).
- High drilling fluid density causing large overbalanced pressure.
- Scraping mud cake provoking pressure surge and increasing formation to mud contact time during bit trips.

Drilling fluid filtrate invasions

Drilling filtrate damage is probably one of the most important cause of production impairment. Liquid phase of drilling fluid contains many potentially damaging compounds. To increase the penetration rate, it is tempting to reduce the fluid loss control of the mud. Higher values of filtrate invasion may result from the deliberate choice of high penetration rates. Sensitive formation are those containing clays that can be dispersed and/ or swollen, or those low permeability rocks in which saturation problems dominate, or those reservoirs producing almost saturated brines or high asphaltine or paraffin content oils.

Factor that enhances drilling fluid invasion include:

- High permeability of the mud filter cake, a result of either poor design of the drilling fluid or detrimental drilling procedures;
- High over balance
- Long formation-to drilling fluid contact time.

Water base mud filtrates may have a long salinity and high pH and may contain dispersants and polymers, water is a cause of in-situ clay and of water blocking I low-permeability rocks dispersants can either aggravate clay problems or precipitate inside pores. Filtrate temperature is less than reservoir temperature thus causes cooling effect. It may cause deposition of paraffin or asphaltene.

Problems of oil base mud are as follows-

- Oil-base muds contain more solids than water-based mud. Consequently .particle invasion is pronounced.
- Oil that invades gas reservoir, especially tight reservoir, causes sharp reduction in relative gas permeability (more problematic than water invasion because oil comparatively higher viscosity and lower vapor pressure of oil).
- Strong oil- wetting surfactants used to disperse solids in oil-base convert formation rocks into a wet state. This significantly reduces the relative permeability to oil.

Cement slurries

Use of filtrate loss agents and broad particles size distribution of cement grains limited the filtrate invasion of cement slurry. In few cases, it may cause permeability impairment which are as follows –

- The relatively high pH of cement slurry filtrates is particularly detrimental to formation clay minerals. Calcium ions liberated by cement particles are very quickly exchanged on clays near of wellbore. The resulting modification of the filtrate composition makes it a perfect destabilizing fluid on terms of dispersing ability.
- Cement filtrate which come in to contact with connate high concentration calcium can provoke precipitation of calcium carbonate, lime or calcium silicate hydrate.
- Over dispersed slurries (with no yield value) present rapid serration of cement particles at the bottom of water at the top of the cement Coolum. Large invasions of free water are likely to take place in this case. The resulting water blockage may be significant.

Squeeze cementing

Squeeze cementing is said to be particularly damaging in consolidated, high permeability sandstones. High pressure is used for squeezing cement are thought to cause formation fracturing and slurry invasion.

Perforation damage

Performance is always a cause of additional damage in formation rocks. Wheather it is performed overbalanced or underbalanced, it always compacts the rock around the perforations averages 80%.

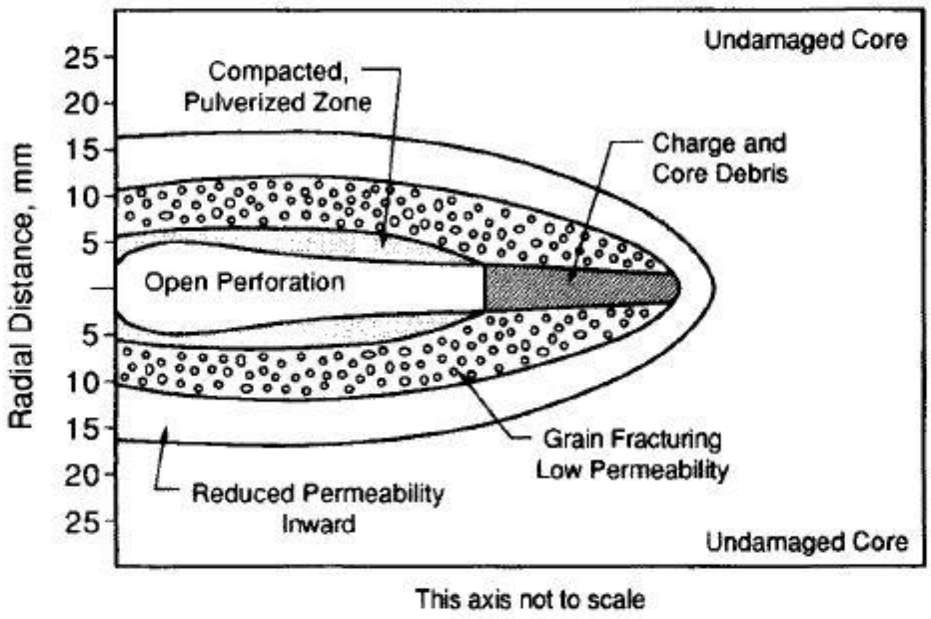


Fig 2.1 – schematic diagram of perforated core showing zones of damage, courtesy: Schechter

There are many other factors that can further reduce productivity.

- Performing overbalance always forces formation and gun debris in to perforation walls and decreases the permeability near the perforations.
- Improper choice of perforation geometry as it relates to formation type:-large diameter, low penetration perforations are preferred in soft rocks tat should be gravel packed ; low diameter high- penetration once are preferred in hard formations.

Completion and work over fluids damage

Various and completion and work over operation also responsible for formation damage

- Permeability impairment of formation rocks and productivity impairment of perforation by suspended solids (including bacteria) and polymer residues.
- Common problems resulting from filtrate invasion: clay swelling and dispersion, water and emulsion blocks, precipitation of scales.

Damage In gravel packs

Main source of damage in gravel packs include-

- Improper placement of the gravel pack (perforation remaining empty or incomplete filling of the annulus between casing and screen), allowing perforation filling by formation sand, pack fluidization and subsequent intermixing of sand and gravel in the case of pressure surges.

- Thread dope, paint, and rust polymer residue forced between formation sand and gravel pack during placement.
- Inadequate gravel size, leading to gravel pack invasion by formation fines during production.

Damage during production

Some reservoir cannot be produced at high flow rate or large drawdowns without being affected by adverse phenomena. Permanent damage which cannot be removed simply by reducing production rate, may be created.

Native silts and clays loosely attached to pore walls can be put into motion by high flow rate especially when two or more immiscible fluids are produced at the same time. These particles can either block pore throats in the vicinity of initial location or either migrate towards well bore.

Reduction in pore pressure during production and sometime cooling resulting from gas expansion, results in precipitation of organic] or organic materials. There are case where they can reduce the formation permeability, seeds such as high specific area clays, promote the deposition of organic materials (especially alphatenes)] or the precipitation of super saturates salt solutions. Common scales are calcium carbonate] and calcium sulphate.

Asphaltene deposition on pore walls may not significantly decrees the formation porosity and absolute permeability. However, through this process the rock tends to become oil wet, which reduces the relative permeability to oil and, under certain conditions, favors the buildup of emulsion blocks if water is simultaneously produced.

Damage during stimulation

Acidizing Treatments

Usual problems already encountered in other phase of the life of a well may also occur during acidizing treatments , especially in cases of inappropriate design . These include:

- Damaging materials from the tubing entering the formation rock.
- Oil-wetting the reservoir by surfactants, especially corrosion inhibitors {112}, which can create emulsion blocks.
- Water blocks
- Asphaltene/paraffin deposition when large volumes of acids are injected.

In addition to these common damaging processes, specific production impairment can also possible from poor design of acidizing treatments. These impairment include the following:

- Sludges produced by reaction between acids and asphaltenes especially in the presence of some additives9 particularly surfactants) or of dissolved iron.
- Deconsolidation of formation rock caused by excessive dissolution of cementing material by acids.
- Precipitation of byproducts from the reaction of acid with formation minerals A third class of byproducts consists of species such as fluosilicates precipitating in the form of individual crystals that can migrate towards pore throats and produce a “long- jam”. Iron sulfide that precipitates, even at very low ph during the acidization of sour wells, is another compound belonging to this category.
- Some sequestring agents added to acids to prevent iron problems can form percipients when the acid is spent and no iron is present.

Methods to enhance productivity ratio:

These methods are as follows-

Acidization:-

Acidization is the process in which acid is injected into the formation, below fracturing pressure. Objective of acidization is dissolution of minerals present in the form of matrix as well as fines which clog pore throat. Consequently, permeability of formation increases. Successful acidizing involves strategic implementation. It requires detailed study of formation mineralogy, compatibility of acid, additives with formation fluid and formation rock. Generally, 15 wt % HCL is used for limestone formation and mixture of 12wt % HCL and 3 wt % HF is used for sandstone formation.

Acid Fracturing: -

It is well stimulation process in which acid is injected into a formation at pressure sufficient to fracture the formation or to open the existing natural fractures. As acid flows along the fracture it etches the face of formation in non- uniform manner. Consequently conductive fracture is created which remains open even after fracture closes, resulting in increment in formation permeability.

Hydraulic Fracturing: -

It is process which is applied to influence large area of reservoir. In hydraulic fracturing process, properly tailored fracture fluid is injected at pressure which create fracture in strata. Certain pressure is maintained to propagate the fracture into formation. In order to keep fracture open even after removal of pressure, propping agents is added into the fracturing fluids. Sand grains, glass beads etc. are some example of proppants.

Hydraulic Fracturing is very expensive operation as a result every possible step is taken to make job efficient and successful.

Chapter 3 Sandstone Acidization-

An acidizing treatment for a sandstone formation will consist of sequentially injecting three fluids: a preflush the hydrofluoric acid-hydrochloric acid mixture (HF-HCl mixture), and an afterflush. Each of these fluids serves a definite purpose.

The preflush is usually HCl ranging in concentration from 5-15 wt% and containing corrosion inhibitors and other additives, as required. The preflush displaces connate water from the near-wellbore region, thereby minimizing direct contact between sodium and potassium ions in the formation brine and the HF or fluorosilicate reaction products, insoluble sodium or potassium fluorides or fluorosilicate. The HCl preflush also reacts with calcite or other calcareous materials, thereby reducing (or eliminating) reaction between HF and $CaCO_3$. This avoids waste of the more expensive HF and prevents precipitation of calcium fluoride (CaF_2). Finally, the preflush may serve to precool the formation.

Following the preflush, an HF-HCl mixture (usually 3 wt% HF and 12 wt% HCl) is then injected. The HF reacts with clays, sand, drilling mud or cement filtrate to improve permeability near the wellbore. The HCl essentially will not react with these materials but is needed to keep the pH low, thereby reducing the precipitation of HF reaction products.

An afterflush is generally applied to isolate the reacted HF from brine that may be used to flush the tubing, to displace spent acid into the formation and to restore water wettability of the formation. Normally, one of three types of afterflush is used: (1) for oil wells, either a hydrocarbon afterflush, such as diesel oil or 15 wt% HCl is used; (2) for water injection wells, HCl is used; and (3) for gas wells, either acid or a gas (such as nitrogen or natural gas) is used. With a liquid afterflush chemicals are usually added to aid in removing treating fluids from the formation, restoring water wettability to formation solids and removing precipitated acid reaction products, and prevention of emulsion formations. When a gas is used as an afterflush, cleanup additives such as surfactants to reduce the surface tension are sometimes added to the HF-HCl stage of the treatment.

Sandstone Matrix Acidizing Theory-

Matrix acidizing is that process whereby acid is injected into a formation at a pressures less than the fracture pressure. The acid is forced into the formation pores in the region surrounding the wellbore. Rock will consequently be dissolved in the invaded region, leaving permeable channels leading into the wellbore to assist the production of oil. This well treatment is normally applied to remove near wellbore damage.

Three important mechanism that contribute to the final productivity of an acidized well include: erosion of the pore structure as the acid flows through these pores, consumption of the acid, and selective dissolution of certain minerals. Erosion of the pore structure leads to both increased porosity and permeability. Rate of acid consumption is an important feature, since this limit the depth to which acid penetrates. Finally the mineral composition in the acidized region depends both on time and distance from the wellbore face because minerals do not react at differing rate. These mechanisms are coupled together. It is not possible to consider them separately. It can be explained in mathematical from using acid balance in porous media.

Study of Sandstone acidization Kinetics using Lumped Reaction Model

According to lumped reaction model all of acid soluble minerals are divided into two categories- fast reacting and slow reaction. Detrital quartz, Detrital Clay, Chert come under slow reacting minerals and Authogenic Clays. Detrital Feldspar and Amorphous Silica comes under fast reacting minerals. An approximate analytical solution of acid mass balance equation is possible if the rate of reaction minerals is much less than fast reacting minerals so that only fast reaction is considered, resulting equation as follows-

$$-u\frac{\partial c_{\mathrm{HF}}}{\partial x} - (1-\phi_0)V_{\mathrm{F}}\alpha_{\mathrm{F}}E_{\mathrm{f}}^{(\mathrm{F})}c_{\mathrm{HF}} = \phi_0\frac{\partial c_{\mathrm{HF}}}{\partial t} \quad \text{……………………………………………………… (3.1)}$$

The following dimensionless variables can now be defined:

$$\psi = c_{\mathrm{HF}}/c_{\mathrm{HF}}^0$$

$$\Lambda = V_{\mathrm{F}}/V_{\mathrm{F}}^0$$

$$\epsilon = x/L$$

$$\theta = t/\tau = tu/\phi_0 L$$

Where L is the length of a linear core and Θ is the number of pore volume injected into the core. Here C^0_{HF} and V^0_F are the initials values of C_{HF} and V_F respectively. The above equation can be written in terms of these new variables as:

$$\frac{\partial\psi}{\partial\theta}+\frac{\partial\psi}{\partial\epsilon}+\left[\frac{(1-\phi_0)V_F^0E_f^{(F)}\alpha_F L}{u}\right]\psi\Lambda=0$$

………………………………………………………….. (3.2)

$$\frac{\partial\Lambda}{\partial\theta}=-\left(\frac{\phi_0\beta_F c_{HF}^0 M_F}{V_F^0\rho_F}\right)\left(\frac{V_F^0E_f^{(F)}\alpha_F L}{u}\right)\psi\Lambda$$

……………………………………………………………… (3.3)

There are two dimensionless parameters appearing in these equations. The Damkohler number is defined as:

$$A_c^{(F)}=\frac{\phi_0\times C_{HF}^o}{(1-\phi_0(Kg-\text{moles of HF per m}^3\text{ of formation}}$$

Acid capacity number = (Mass of minerals dissolved per unit volume) / (Mass of minerals present per unit volume)

Calculation of Permeability of acidized zone -

Approach that has been used in the design of acidization is based on the empirical equations that have been derived by experiments on very porous material like sintered glass. Berea sandstone etc. once the damage is removed the n there is further increase in permeability. Thus it is important to establish the zone in which damage in the form of particles clogging the pore throats has been cleared. Here we assume that damage removal is accomplished for all $\epsilon < \epsilon_f$, where ϵ_f is the frontal position. The zone behind the front has a permeability k_A (the A denotes acidized), whereas downstream of the front the permeability is K_s. The average permeability in core is given by-

$$\frac{\bar{k}(\theta)}{k_S}=\frac{1}{\int_0^1\frac{k_S\,d\epsilon}{k}}=\frac{k_A}{\epsilon_f k_S+(1-\epsilon_f)k_A}\qquad(\text{for }\epsilon_f<1)$$

………………………..(3.4)

The mean permeability (k), which is the average value obtained by measuring the pressure drop across the entire length of the core, depends on the position of the front. Upstream from the front, the fast reacting minerals have been removed. The porosity has been increased by virtue of their removal. Since V% is the volume of the fast-reacting minerals per unit volume of minerals, the increase in porosity is given by:

$$\phi_0-\phi=V_F^0(1-\phi)$$ ………………………………………………. (3.5)

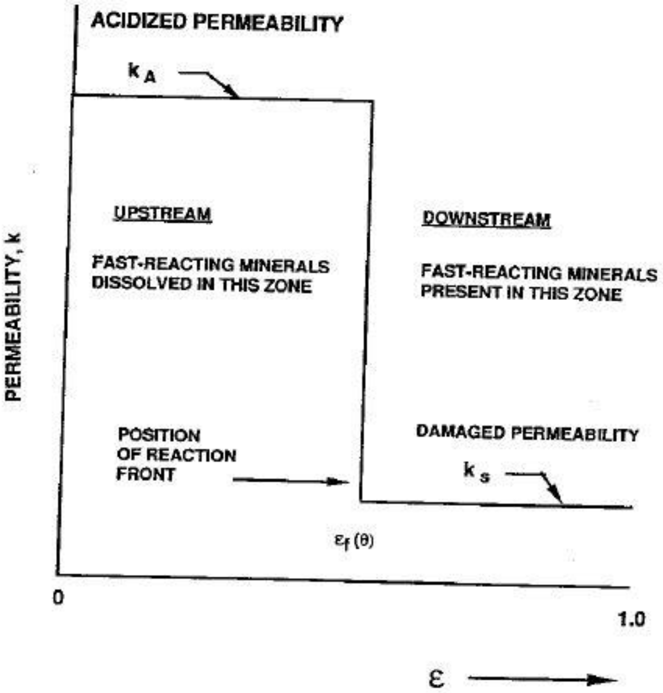


Figure 3.1 permeability as function of position in linear system, courtesy: Schechter

Characteristics of the slow reaction zone-

The general features governing the design of a matrix acidizing treatment can best be visualized by first considering the penetration of acid into a core whose solid matrix is composed entirely of a slow reacting substance, say, quartz. Since the volume of the slow reacting solid is large, then the acid capacity number of the slow reacting quart (A_C^S) tends to zero. It is observed in the limit of small acid capacity numbers.

$$\Psi = e^{-\left[Da^{R,S} Ef(R) \right]} \text{……………………………………………………………………} (3.6)$$

This equation is interesting since it suggest that the acid concentration depends on the distance measured from the core inlet, but does not depend on o, the number of PV injected. This implies that the effluent concentration from a core should be constant once the fast –reacting minerals have been removed as shown in figure 4.2 and 4.3. The second segment is practically horizontal indicating that for this particular Berea sample the effluent concentration becomes essentially constant, independent of o once the fast-reacting materials have been removed. A number of experiments on Berea all show similar behaviour.

We expect that acidization carried out in the field will exhibit similar behaviour. Thus it is worthwhile to investigate the implication of equation (8) in somewhat greater detail.

If it is desired to increase the acid penetration distance, the Damkohler number for the slow-reacting minerals must be reduced. The only variables that are available to the experiment are the temperature, the acid concentration and the acid flux. In order to reduce Damkohler number core temperature can be reduced using adequate preflush volume. Consequently acid penetration distance increase.

The Damkohler number is independent of the inlet acid concentration, so that increasing it will not change the position at which Ψ takes on a particular value. Of course for fixed Ψ the acid concentration increases as the inlet acid concentration increase. There are varieties of reason for which increasing the concentration of HF excess of some minimum level may be undesirable.

The Damkohler number can also be increased by increasing the acid flux. In core tests u can be varied over a wide range; however, in matrix acid treatments the acid flux is limited by the fracture gradient.

Equation (5) is a key result for the design of matrix acid treatments. It shows that there is a limit to the depth surrounding the wellbore from which damage can be removed by acid.

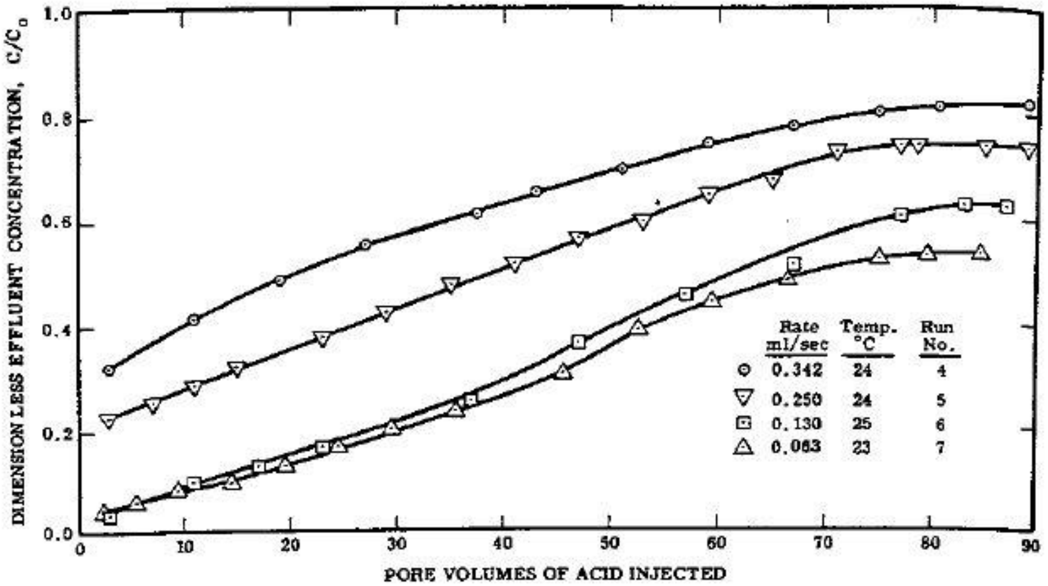


Figure 3.2 Plotted data of effluent acid concentration as a function of PV injected for Berea Sandstone. The various curves show the effect of the flow rate, courtesy: Schechter

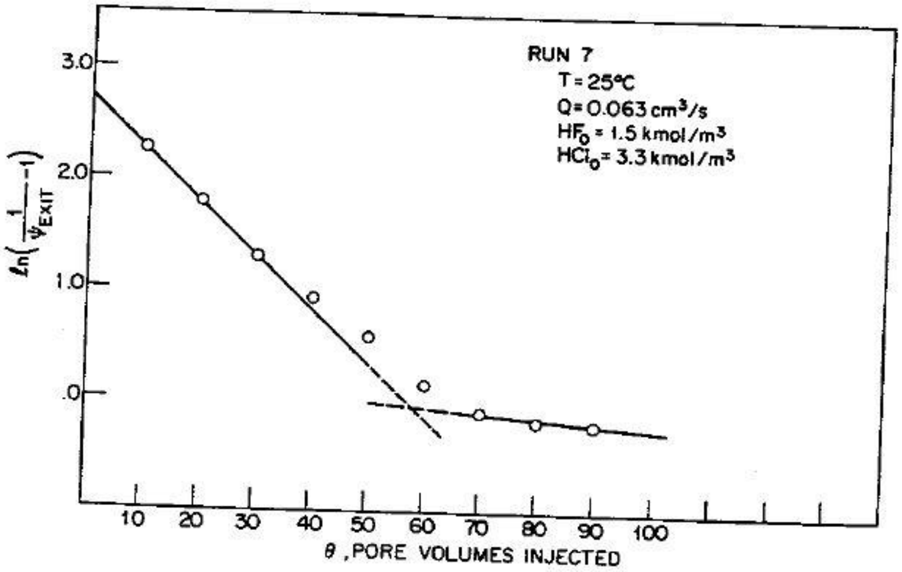


Figure 3.3 The effluent HF acid concentration for an injection rate of 0.063 cm3/s replotted from Fig 3.2 to show the reaction zones (With permission of American Institute of Chemical Engineers), courtesy: Schechter

Speed of the fast-reacting mineral Front-

Effluent acid concentration in two extreme cases –one for which the system contains only a small quantity of fast reacting mineral with the remainder of the solid matrix being composed of an inert solid, and at the other extreme, one which is composed entirely of a single slow reacting mineral have been discussed. The interaction is illustrated by curve shown in fig 4.4. The fast reacting mineral is shown to exhibit a reaction front shaped much the same as that where there is no slow reacting mineral. The difference between the reacting zones is in the acid concentration. Because of the presence of a large quantity of the slow reacting mineral, the acid concentration decreases continuously from the core inlet until it reaches the reaction the reaction zone where quantities of fast reacting mineral remain. At this point the acid concentration decreases rapidly causing the fast reacting front to advance.

Let us define ϵ_f as the position of the reaction front and consider rate at which this front moves. As ϵ_f increases, the concentration of acid arriving at the front will decrease in accordance with equation (8). The acid concentration decreases at the front, the velocity of the front will also decrease since the dissolving power of acid is directly proportional to the concentration of acid. Thus because the acid must flow through a porous medium of slow reacting mineral to reach the reaction front, a portion of the acid dissolving power of the acid is lost. Clearly a fast-reacting mineral cannot be removed for a distance beyond acid penetration distance.

To complete those concepts needed for a rational design, the frontal position (ϵ_f) as a function of the PV injected must now be calculated.

To do this calculation it is noted the front moves at a rate dictated by the acid capacity number. To account for the reduced acid concentration as the acid arrives at the front as shown by fig 4.4, gives:

$$\theta^{(R)} = \frac{\exp(D_a^{(R,S)}\epsilon_f^{(R)}) - 1}{A_C^{(F)} D_a^{(R,S)}} + \epsilon_f^{(R)} \quad \text{………………………………………………………. (3.7)}$$

This expression is the desired one. It relates the number of PV injected to the position of the front. There are two parameters that appear the Damkohler number for the slow reacting mineral. The Damkohler number for the fast reaction is a third important variable. If it is sufficiently large, it is possible to assume the front to sharp. The acid capacity number for slow reacting mineral is small (A_c^S) tends to zero and is not needed in the design of an acid treatment. Equation (11) can be used to calculate A_c given Damkohler and the point of intersection between the to line segments in fig 4.3. At this intersection it can be assumed that e_f=1, i.e. this is the number of PV (Ɵ), at which the front emerges from the core.

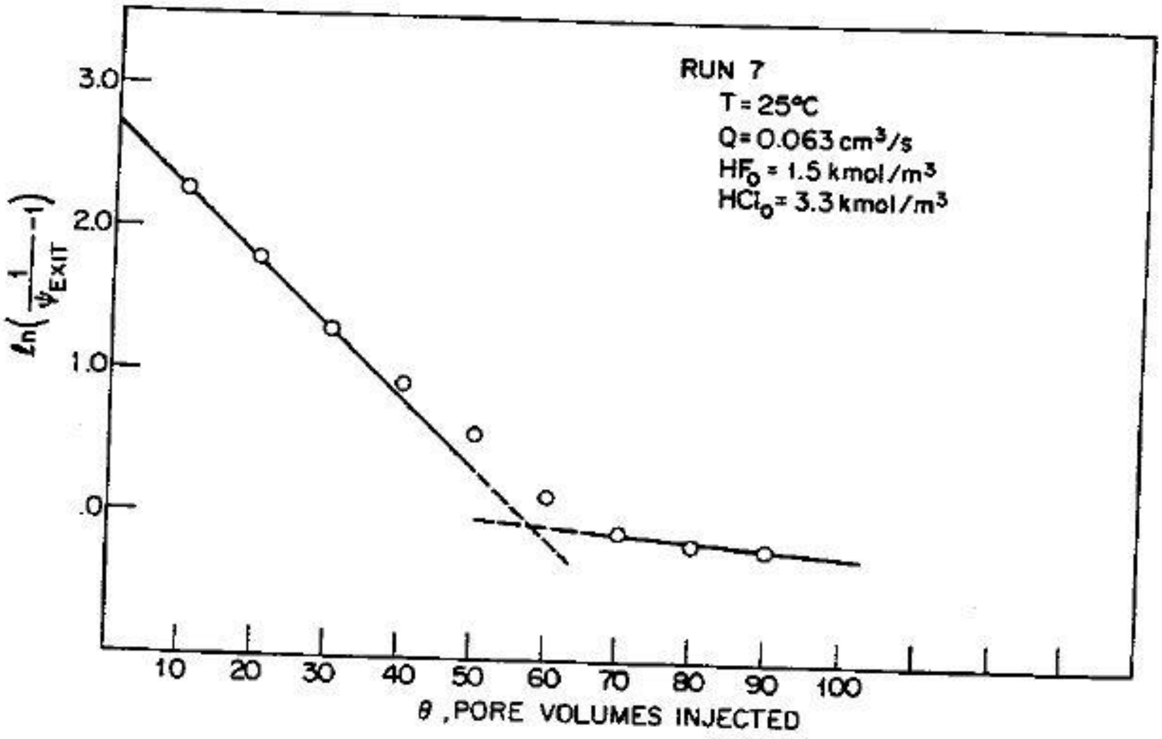


Figure 3.4 Graph showing intersection of two mineral front. The acid concentration is plotted as function of position for the case of fast reacting minerals and slow reacting minerals. , courtesy: Schechter

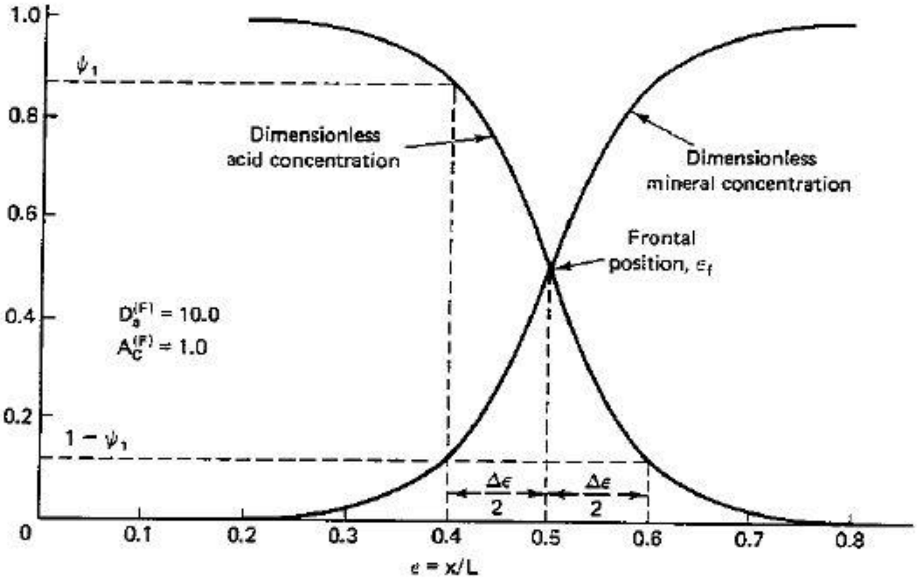


Figure 3.5 Detail structure of the reaction zone shown for single fast reaction, courtesy: Schechter

Selection of Additives for Acidization Design:-

Matrix acidizing is a complex chemical process and therefore it is necessary to include some additional chemicals for achieving the objective of damage removal with minimizing the side effects. For the same reason it is necessary to include some additives in the required acid solution. Some of the commonly added acid additives are-

- Corrosion inhibitors
- Surfactants
- Diverting agents
- Anti-sludge agents
- Iron controllers
- Mutual solvents: and
- Clay stabilizers

These additives are intended to-

- To divert acid flow from more permeable, undamaged zones permeable ones thereby allowing a more uniform treatment.
- To prevent corrosion of wellbore tubular goods
- To form complexes with iron, to prevent precipitation
- To reduce friction drop through tubular goods; and
- To eliminate emulsions and sludging in certain highly asphaltic oils.

Corrosion inhibitors

The most important acid additives are corrosion inhibitors, if high bottom hole temperature are encountered or long acid pipe contact times are anticipated the choice of the acid itself is governed by the selection of the most economical means for controlling corrosion and still accomplishing the goals established for the treatment.

Any metal surface is composed of electrodes, as long as this metal remains dry the electrical circuit remains short circuited but on exposure to acid solution local action cells starts functioning and is accompanied by chemical conversion of metal to corrosion products.

A compound used as inhibitors requires a favourable polar group or a group by which the molecule can attach itself to that metal compound, these includes nitrogen, sulphur, alcohol or an amine compound. Commercially used inhibitors are complex organic compounds.

Factors effecting corrosion during an acid treatment are

- Temperature
- Contact time
- Acid concentration
- Metal type: and
- The corrosion inhibitor used
- Degree of agitation
- Metal to acid volume ratio
- Gas composition if an interface is present
- Presence of other additives such as surfactants

These factors are taken into account by laboratory evaluation of Meta surface exposed to the corrosion inhibitor to be used in the treatment. The metal coupon is inserted into a heated pressure vessel containing the acid and the corrosion inhibitor to be used, the amount of corrosion is measured by the weighing the metal coupon and after the test.

Agitation increases the corrosion rate, thus if mass transfer is a limiting factor effect of agitation may be pronounced. At low levels of agitation corrosion rate decreases and at high levels corrosion rate increases, thus it is recommended that oxygen should be excluded from the test bubbling nitrogen through the acid solution.

The effectiveness of a given corrosion inhibitor also depends on the metal and the acid type and for the same reason formic or acetic acid is used in deeper hot wells because it is difficult to inhibit the corrosion of hydrochloric acid at these conditions. Any additive that alters the tendency of corrosion inhibitor to absorb on the metal surface like that of surfactants, mutual solvents also affects its effectiveness in the given acid solution.

Surfactants: - Surface active agents are used in acid solution to-

- Demulsify spent acid and oil
- Reduce interfacial tension
- Speed clean up: and
- To prevent sludge formation

Surfactants should never be added to the acid solutions without the understanding of their effect evaluated at reservoir condition on live crude. Generally anionic or non-ionic surfactants are preferred for use in acid solution for use in acid solution. The surfactant added to the acid solution should not reduce the effectiveness of corrosion inhibitor being used and thus fluorocarbon surfactants may be the best choice concerning this issue provided that it serves other purpose well too.

Chapter 4 Designing Calculations for Selective Case

Designing of sandstone acidization.

Designing of acidization comprises of following

a) Preflush Volume

b) Acid treatment

c) Afterfiush

d) Acid additives

Preflush Volume

The preflush is an important feature of a sandstone acid treatment. The main purposes of the preflush are as follows-

- To remove those formation materials which will react to a significant extent with HF, to displace those formation waters containing ions (Na+, Ca4” +, etc.) which will tend to precipitate with HF.
- To cool the formation in order to obtain deep penetration of acid.
- To displace the iron present as minerals siderite and ankerite, iron can precipitate from spent acid solutions to yield a damaging amorphous gel.

To accomplish these purposes, a large volume of preflush seems to be desirable. Larger volumes should ensure better contact of the preflush with the formation materials, better removal of undesirable reaction products from the near-wellbore region, and more efficient cooling of the formation near the well-bore. By diluting 15 wt% HCI acids to obtain 7.5 wt% solutions, one can increase the volumes of fluid used without substantially increasing the cost and perhaps ease the task of inhibiting the corrosion.

If corrosion is a substantial problem, preflushing with formic acid is acceptable. Because of incomplete reactions, higher molecular weight organic acids are not recommended.

To ascertain the volume of preflush that should be used in a given situation, all HCI soluble components must be removed from the near-wellbore region that is to be treated by the HF-HCJ mixture. Thus, the volume of preflush is a function of the penetration depth of the main HF-HCI acid treatment and the volume fraction of acid-soluble minerals residing in that zone.

Preflush volume is function of porosity, composition of formation and depth of damage (generally 1 feet).

Preflush volume = $\pi(R^2 - R_w^2)$ *H*(1-ϕ)* (percentage of carbonate mineral)……(5.1)

R = Depth of damage radially

R_w = Radius of well

H = Height of formation

ϕ = Average porosity of formation

Acid Treatment

Designing of acid treatment includes rate of injection, composition of mixture, volume of mixture. There is little advantage to be gained by acidizing an undamaged formation. Consequently, it is essential to restrict the injection rate and injection volume such that acid used to dissolve rock in damage zone. Thus it seems self-evident that given a volume of acid, the optimal application will be to dissolve rock in the damaged zone. Acid reacted in the regions beyond the damaged zone will be of little utility. Thus, the injection rate should be adjusted to ensure that the overwhelming bulk of the acid is spent within the damaged region.

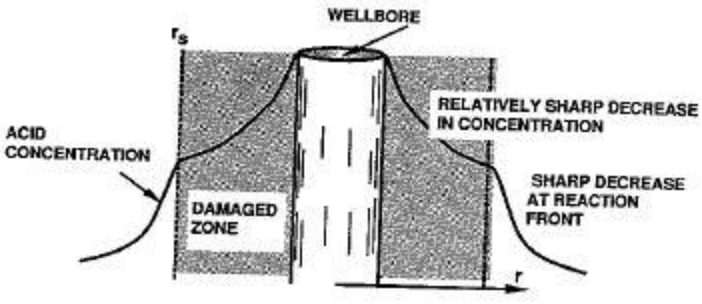
In addition to restricting the reaction of acid to the damaged zone, the design strategy imposed here also requires that the amount of acid expended in removing the slow- reacting minerals be minimized because if the damage is caused by debris dislodged from the rock surfaces it is almost certainly composed of fast-reacting minerals. Furthermore fines from drilling, completion, or cementing fluids that have entered the pore spaces and clogged the pore throats are also likely to be highly reactive with HF if they react at all. Thus, the strategy of most efficiently removing the fast-reacting minerals from the damaged zone appears to be a logical one even though experimental evidence proving this to be the case does not now exist.

Optimum acid injection rate will be different for each acid treatment. An optimum value of a dependent variable exists as a compromise between competing forces. In this case a slow injection rate will yield a sharp reaction front, as shown by Fig. 4. 1(a) and little of the fast-reacting minerals will be dissolved beyond the damaged zone. Because the injection rate is slow, however, the acid experiences a long contact time with the slow-reacting minerals behind the front and much of it is spent in unfruitfi4 reactions with these minerals.

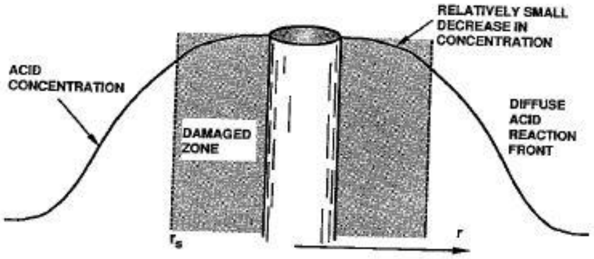
If the injection rate is increased, then the amount of acid reacting with the slow-reacting minerals is correspondingly decreased as shown by Fig. 4.1(b), but now the reaction front may become diffuse and unwanted reaction with the fast-reacting minerals beyond the damage zone may take place.

The amount of acid required to remove most of the minerals from the damaged zone will be a minimum when the injection rate is fixed at the optimum value It should be noted that in some cases the optimum injection rate will maximum one permitted and therefore these treatments are simply designed based on the maximum allowable rate. In this case it would be helpful to measure the bottomhole wellbore pressure during the treatment so that as damage is removed and the wellbore pressure declines, the rate can be adjusted upward to more nearly approach the optimum value.

The depth of the damaged zone is rarely known, and most acid treatments are designed by first selecting a given vaolume of acid to be used. Associated with this volume is an optimum injection rate. According to the strategy defined here, it can be argued that small volumes correspond to small injecton rates.



CASE A: SLOW INJETION RATE



CASE B: FAST INJECTION RATE

Figure 4.1 Schematic diagram showing effect of acid injection rate has upon acid concentration and reaction front. The profile of acid injection composition will depend on the injection rate, (A) Slow injection rate; Large decrease in concentration in the zone behind the front and sharp front, (B) Fast injection rate: Small decrease in concentration in the zone behind the front and diffuse front, courtesy: Schechter

Rate of Acid Injection - Injection rate should be such that pressure against sandface less than fracture pressure.

Fracture pressure = (Fracture Gradient)*(Depth of formation)

Fracture pressure = (FG)*(Depth of formation)

Maximum injection rate can be obtained by using following equation:

$$P_{wf} - P_R = \frac{i\mu}{2\pi kh}\left[\ln\left(\frac{r_e}{r^1 w} - \frac{3}{4}\right)\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.1)$$

P_{wf} = Injection pressure (FG*D)

P_R = Reservoir pressure

μ = Viscosity of acid mixture

r_e = Drainage radius

r_w = Radius of well

r'_w = Effective wellbore radius

K= average permeability

H = Thickness of formation

S = skin

Injection rate of acid mixture must be less than maximum injection rate. Above maximum injection rate formation will be fractured. In addition to maximum injection rate constraint, rate of injection should be optimal. Using Damkohler's number, rate of injection for fast reacting minerals and slow reacting minerals can be determined. Optimal injection rate is one which satisfies dissolution of both fast reacting minerals and slow reacting minerals. An accurate estimate of this quantity is quite difficult to obtain without experimental data. Unfortunately these data are rarely available. Damkohler numbers for Berea and for a Phacoides sandstone are available. As a crude estimate a scaling procedure is recommended as follows

$$Da(R_1F) = \frac{Da^{(F)}{}_B V_F^0 (1-\phi_0) E_f(T) u_\beta \pi r \omega^2 h}{\left(V_F^0\right)_\beta (1-\phi_0)_\beta E_f(T_\beta) L_\beta i} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.2)$$

The subscript B denotes values obtained using Berea or any other standard linear core test. Petrographic and X-ray analyses of representative samples of the Berea cores that were acidized to obtain the results). Clay (illite and chlorite) is present as rock fragments and thus is classified together with quartz as a slow-reacting mineral. Once the carbonates are removed, then petrographic analysis shows $(V^\circ_F)_B = 0.052$ *and* $(1 - \phi)_B = 0.79$.

It also consist of rate function dependent on temperature.

Reaction front inside formation should be sharp enough to satisfy the dissolution of slow reacting and fast reacting minerals then the required Damkohler number is:

$$Da^{(R,F)} = \frac{\ln\left[(\frac{1}{\Psi_1}) - 1 \right]}{\delta\left(Ef^{(R)} + 1\right)} \cdots\cdots\cdots\cdots\cdots\cdots \text{(5.3)}$$

Where $\psi = C_{HF}/C_{HF}^{o}$

$\delta = \Delta r/r_f$

Δr = Width of zone

r_f = Distance travelled by front

$$Da^{(R_1S))} = Da^{(S))}\left(\frac{u}{L}\right)\frac{E_f^{(s)}(T)}{E_f^{(s)}(298)}\left(\frac{\pi r\omega^1}{\frac{j}{h}}\right) \cdots\cdots\cdots\cdots \text{(5.4)}$$

Using Damkohler's number for slow reacting mineral, the acid concentration at the reaction front can be determined by following equation:

$$\Psi = e^{-\left[Da^{R,S} Ef^{(R)}\right]} \cdots\cdots\cdots\cdots\cdots\cdots \text{(5.5)}$$

Second step toward designing of job is calculation of acid volume. It requires determination of Acid capacity number:

$$A_c^{(F)} = \frac{\phi_0 \times C_{HF}^{o}}{(1 - \phi_0 (Kg - \text{moles of HF per m}^3 \text{ of formation})} \cdots\cdots\cdots \text{(5.6)}$$

Using Acid capacity number and Damkohler's number pore volume (acid mixture) being injected into the formation can be determined by:

$$\theta^{(R)} = \frac{\exp\left[Da^{(R,S)} Ef^{(R)}\right] - 1}{A_c^{(F)} Da^{(R,S)}} + Ef^{(R)} \cdots\cdots\cdots\cdots\cdots \text{(5.7)}$$

The equation also relates the pore volume for the radial system to the penetration depth. It determines volume utilized by unit pore volume. Consequently, for specific damage length, volume of acid injection can be determined by:

$$\theta^{(R)} = \frac{it}{\pi r_w^2 h \phi_0} \quad \text{(5.8)}$$

Where, i = Rate of acid injection

T= Time of acid injection

End result of acidization job is increment in productivity ratio. Productivity ratio depends upon permeability which finally depends upon porosity.

$$S = \left(\frac{K}{K_S} - 1\right)\ln\left(\frac{rs}{rw}\right) \quad \text{(5.9)}$$

$$\frac{J_A}{J_D} = \frac{\ln\left[\frac{re}{rw(A)}\right]\frac{-3}{4}}{\ln\left[\frac{re}{rw(D)}\right]\frac{-3}{4}} \quad \text{(5.10)}$$

Where

$r_w'^{(D)}$ = Effective well bore radius of damaged zone

$r_w'^{(A)}$ = Effective well bore radius of acidized zone

Generally, composition of acid mixture for acidization of sand stone l2wt% HCL and 3wt% HF. It is also known as Mud Acid. Hydrochloric acid is used to keep the pH high, as low pH result in precipitation of insoluble reaction product. Composition of acid mixture should not cause damage to formation due to precipitation product of reaction. Consequently, acid mixture is function of formation mineralogy, dissolving power of acid and desired increment in productivity ratio. Additives like corrosion inhibitors, surfactants etc. are added to make process efficient.

CHAPTER 5: CASE STUDY FOR SANDSTONE ACIDIZATION

Radius of the Wellbore	=	0.15 m
Radius of damaged zone	=	0.3048 m
Drainages radius of well	=	300 m
Height of payzone	=	5 m

Average permeability of formation (K_{avg} = 90 md)

Skin = +6

Porosity (ϕ) = 0.20

Formation depth = 2000m

Fracture gradient = 18 kpa/m

Average reservoir pressure = 6500 kpa

Composition of formation

Mineral	**Volume (%)**
Calcite	6
Siderite	4
Quartz	75
Orthoclase	6
Kaolinite	5
Montmorillonite	4

We will design the following:

a) Preflush Volume

b) Acid Treatment

c) After Flush

d) Additives required

Finally we will discuss the effect on productivity of well after the matrix acidization treatment.

Steps for Acidization design:

a) Preflush Volume Design: Preflush is required to remove materials which will react with HCl and to remove Na^+, Ca^{2+} which will precipitate with HF.

- We will use 7.5 weight% HCl solution as preflush.

Volume of carbonates per metre of the formation

$= \pi (r^2 - r_\omega^2) (1-\phi) f$

$= \pi [(0.3048)^2 - (0.15)^2] [(1-0.20)(0.10)]$

$= 0.017 m^3/m$ of formation.

Where, r = damage radius (m) = 0.3048m

r_ω = Wellbore radius (m) = 0.15m

f = volume fraction of acid soluble mineral

= 0.06 + 0.04 = 0.10

Dissolving power calculation:

$$2HCL + CaCO_3 \rightleftharpoons Cacl_2 + H_2O + CO_2$$

Gravimetric dissolving power (β):

$$\beta = \frac{1}{2}\left(\frac{Moles\ of\ CaCO_3}{Mole\ of\ HCl}\right)\left(\frac{Mol.wt.of\ CaCO_3}{Mol.wt.of\ HCl}\right)\left(\frac{Mass\ of\ HCl}{Mass\ of\ acid\ solution}\right)$$

$$= \frac{1}{2}\left(\frac{100}{36.5}\right)\left(\frac{7.5}{100}\right)$$

$$= 0.102$$

$$\text{Volume of preflush} = \frac{\text{Volume of acid soluble minerals (carbonates) per metre of formation}}{\text{Volumetric dissolving power of Acid solution}}$$

Now Volumetric dissolving power (X) of 7.5 Wt. % of HCl

$$X = \frac{\beta * \rho acid}{\rho CaCO_3} = \frac{(0.102)(1.0376)}{2.71} \approx 0.40$$

$$\text{Volume of preflush} = \frac{0.017}{0.040}$$

$= 0.42m^3$ per metre of formation

Hence,

Total Preflush volume = 0.42 x depth of formation

= 0.42 x 5

Preflush Volume = 2.1 m^3 of 7.5 wt. % HCl Solution

b) Acid Treatment

In this case the amount of orthoclose and montmorillonite is small, hence we will reduce the concentration of HF to reduce $Si(OH)_4$ precipitation.

Acid → 1.5 wt% HF and 12 wt% HCl

Treatment temperature: It is recommended to use 55ºC (After cooling around wellbore), since from back calculation we found that optimum injection rate exceeds maximum injection rate beyond 60ºC temperature.

Radial Damkohler number for slow reacting mineral

$$Da^{(R_1 S))} = Da^{(S))}\left(\frac{u}{L}\right)\frac{E_f{}^{(s)}(T)}{E_f{}^{(s)}(298)}\left(\frac{\pi r \omega^1}{\frac{i}{h}}\right) \text{-- Eq. 1}$$

Where $Da^{(S)}$ = Damkohler number for Linear core

$E_f{}^{(s)}$ = Average forward reaction rate for slow reaction.

u = velocity

L = length of linear core

The recommended value for:

$Da^{(S)}$ = 0.62

$\frac{u}{L}$ = 0.00124 sec^{-1}

$$\frac{E_f{}^{(s)}(T)}{E_f{}^{(s)}(298)} = \exp\left[-1150\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$= \exp\left[-1150\left(\frac{1}{328} - \frac{1}{298}\right)\right] = 1.41$$

Putting in Eq. 1

$$Da^{(R_1S)} = (0.62)(1.24\times10^{-3})\times(0.15)^2(1.40)\frac{h}{i}$$

$Da^{(R_1S))} = \frac{h}{i}(7.65\times10^{-5})$ -- Eq.2

The optimal injection rate also depends on the radial damkohler number for fast reacting mineral. However in absence of experimentl data we will take Berea sandstone data.

$Da(R_1F) = \frac{Da^{(F)}{}_B V_F^0(1-\phi_0)E_f(T)u_\beta \pi r\omega^2 h}{(V_F^0)(1-\phi_0)_\beta E_f(T_\beta)L_\beta i}$ --------- Eq.3

$Da^{(F)}{}_B$ = Damkohler number for fast reacting mineral for berea sandstone.

V_F^0 = Volume of fast reacting mineral per unit volume of minerals.

→ $V_F^0 = \frac{0.06+0.04}{0.90} = 0.111$

ϕ_0 = Modified porosity after acidization.

Now : $\phi_0 - \phi = V_F^0(1-\phi)$

→ $\phi_0 = \phi + (0.111)(1-\phi) = 0.288$

- Once the carbonates are removed by preflush, from the data of Berea Sandstone:

$$(V_F^0)_B = 0.052, (1-\phi_0)_B = 0.79, (Da^{(F)})_B = 2.76$$

- Also the rate expression will be choosen according to fast reacting mineral orthoclase.

$$\frac{E_f(T)}{E_f(298)} = \exp\left[-4680\left(\frac{1}{328}-\frac{1}{298}\right)\right] = 4.17$$

- Now for fast reacting mineral radial damkohler number can be calculated from Eq. 3:

$$Da(R,F) = \frac{(2.76)(0.111)(4.17)(1.24\times10^{-3})\times(0.15)^2(0.712)}{(0.052)(0.79)}\left(\frac{h}{i}\right)$$

$Da(R,F) = (6.17\times10^{-4})\frac{h}{i}$ -- Eq.4

- Since the radius of damaged zone is r_s = 0.3048. The reaction Front is required to reach a position.

$E_f^{(R)} = \left(\frac{r_s}{r_w}\right)^2 - 1$ --- Eq.5

Where $E_f^{(R)}$ reaction front position

From Eq. 5, Value of $E_f^{(R)}$ =3

- The experiments on core sample have shown that, to maintain a sharp reaction front, reaction zone width = 0.30 and $\Psi_1 = 0.75$

Then $Da^{(F)} = -\frac{\ln\left[\frac{1}{\Psi_1}-1\right]}{\delta\left(Ef^{(R)}+1\right)}$ -- Eq.6

Ψ_1 = Acid concentration ratio on upstream side = 0.75

δ = reaction zone width = 0.30 m

$Ef^{(R)}$ = 3

On Solving Eq.6, we get $Da(R,F) = 0.916$

From Eq. 4 and Eq. 6: -

$$(6.17\times10^{-4})\frac{h}{i}=0.916$$

$$\frac{i}{h}=(6.74\times10^{-4})\frac{m^3}{m-\sec}$$

Note: The optimum injection rate must be less than maximum injection rate.

Calculation of Maximum Injection Rate:

$P_{wf}-P_R=\frac{i\mu}{2\pi kh}\left[\ln\left(\frac{r_e}{r^1w}-\frac{3}{4}\right)\right]$ --- Eq.7

μ = Viscosity of acid solution

r_w^1 = Effective wellbore radius

i = Maximum injection rate

r_w^1 = $r_w e^{-s} = 3.718 \times 10^{-4}$ m

μ = 9×10^{-4} kg/m. sec.

K_w = $K^*K_{rw} = (90 \times 0.60)(9.87 \times 10^{-16}) = 5.32 \times 10^{-14} m^2$

P_{wf} = $(F.G)(D) = (18 \times 10^3)(2000) = 36 \times 10^6$ pa

P_R = 6500 kpa = 6.5×10^6 kpa

By solving Eq.7

$$\left(\frac{i}{h}\right)_{\max}=(8.52\times10^{-4})\frac{m^3}{m-\sec}$$

Here we see that optimum injection rate is lesser than maximum injection rate.

Hence accepted value of injection rate

$$\left(\frac{i}{h}\right)=(6.74\times10^{-4})\frac{m^3}{m-\sec}$$

Acid concentration at Arrived Reaction Front:

$$\Psi=e^{-\left[Da^{R,S}Ef^{(R)}\right]}$$

$$\Rightarrow\Psi=e^{-[0.113\times3]}=0.712$$

$$Da^{(R,S)}=\left(\frac{h}{i}\right)(7.65\times10-5)=0.113$$

Calculation of Acid Capacity Number:

$$A_c^{(F)} = \frac{\phi_0 \times C_{HF}^o}{(1-\phi_0 (Kg - \text{moles of HF per m}^3 \text{ of formation}}$$

Stoichiometric coefficient for various reaction:-

	B
HF – Muscovite	0.042
HF – Montmorillonite	0.018
HF – Illite	0.018
HF – Kaolinite	0.031
HF – Orthoclase	0.050
HF – Quartz	0.167

Since orthoclase and Quartz are only fast reacting mineral.

Mineral	**Density (Kg/m^3)**	**Volume fraction**	**Mass (Kg)**	**Kg moles**	**β**	**Kg. Moles of HF per m^3 of Formation**
Mont-morillonite	2400	0.04	96	0.106	0.018	5.925
Orthoclase	2600	0.06	156	0.561	0.050	11.22

Total kg.moles of HF required per m^3 of formation = 11.22 + 5.925 = 17.14 Kg.moles.

Now Acid Capacity Number:

$$A_c^{(F)} = \frac{(0.288)(0.81)}{(0.712)(17.14)} = 0.019$$

$$\Rightarrow A_c^{(F)} = 0.019$$

Calculation of Pore Volume (θ^R) To Penetration Depth:-

$$\theta^{(R)} = \frac{\exp\left[Da^{(R,S)} Ef^{(R)}\right] - 1}{A_c^{(F)} Da^{(R,S)}} + 3$$ -- Eq.8

Using $A_c^{(F)}$ = 0.019 and $Da^{(R,S)}$ = 0.113 and Solving Eq.8 We get :

$\theta^{(R)} = 190.9$

- Now $\theta^{(R)} = \frac{it}{\pi r_w^2 h \phi}$ --- Eq.9

From Eq.8 and Eq.9, we calculate:-

$\Rightarrow \frac{it}{h} = 2.69 m^3$

Where $\frac{it}{h}$ = Volume of Acid treatment per metre of formation.

$\therefore$ Volume of Acid treatment = 2.69 m^3

Calculation of Treatment Time:-

We know $\frac{it}{h}$ = 2.69 m^3/m

and $\frac{i}{h}$ = (6.74 x 10^{-4}) m^3/m-sec.

$$\Rightarrow t = \frac{(2.69)}{\left(\frac{i}{h}\right)}$$

$$\Rightarrow t = 3990\, Sec$$

Injection Time = 3990/60 = 66 minutes.

Calculation of New Productivity:-

$$S = \left(\frac{K}{K_S} - 1\right)\ln\left(\frac{rs}{rw}\right)$$

$$6 = \left(\frac{K}{K_S} - 1\right)\ln\left(\frac{0.30}{0.15}\right)$$

$$\therefore \left(\frac{K}{K_S}\right) = 9.656$$

After Stimulation: ϕ final = $\phi_2 + (1-\phi_i)(0.008+0.08)$

$$= (0.20) + (0.80)(0.16)$$

$$\phi_{Final} = 0.328$$

Now; $\frac{K}{K_0} = \exp\left[M\left(\frac{\phi - \phi_0}{\Delta\phi}\right)\right]$

For Sandstone $\frac{M}{\Delta\phi}$ = 45.7 gives best result.

Hence; $\frac{K}{K_0} = 347$

New Skin after Treatment:

$$S = \left[\frac{\frac{K}{Ks}}{\frac{K}{K_O}} - 1\right]\ln 2$$

$$\therefore S = \left[\frac{9.656}{347} - 1\right]\ln 2$$

$$S_{new} = -0.67$$

Calculation of Stimulation production ratio:-

Effective Wellbore radius (Damaged)

r_w (D) = (0.15) e^{-6} = 3.178 x 10^{-4}m

Acidized Wellbore radius

r_w (A) = (0.15) $e^{-(-0.67)}$ = 0.293m

$$\frac{J_A}{J_D} = \frac{\ln\left[\frac{re}{rw(A)}\right]\frac{-3}{4}}{\ln\left[\frac{re}{rw(D)}\right]\frac{-3}{4}} = \frac{13}{6.18} = 2.10$$

$$\frac{J_A}{J_D} = 2.10$$

Where J_A = Acidized productivity Index

J_D = Damaged Productivity Index

RESULT: The Acidization Treatment will double the current well production.

C) Acid placement Techniques/ Diverting Technique: -

Diverting agents are small particles that can be added batch wise to the treatment fluid to temporarily plug the selected zones. Following diverters can be used-

- Reverse Cups and Stradle Packers - There are used for zonal isolation, so that acid can be preferentially sent to the required zone.

- Ball sealers - There are small rubber balls which are pumped with the acid. They sent into the perforation and divert the acid into lower permeability zone.

- Use of Chemical techniques-

  Benzoic acid powder is pumped, which forms filter cake around wellbore providing resistance to flow and hence directing the acid.

  Gelled Acid – These are pumped with main acid solution which will move preferentially to higher permeability zones and divert the main acid to lower permeability zones.

Selection of Diverting Agent:-

- Reverse cups and packer are not beneficial to use since height of the payzone is only 5m.

- Ball sealer works efficiently for high injection rate matrix acidization. In our case, the injection rate is low which makes ball sealer poor diverting agent.

- Choice of Benzoic acid powder as chemical diverting agent is best recommended from the economics point of view.

D) Additives:

1. Iron controllers: - Most of the mineral containing Ferric ions will react during acidization to form ferric hydroxide precipitates. Citric acid/ acetic acid buffer or ethylene-diaminetetraacetic acid (EDTA) can be used as sequestering agents.

2. Anti-sludge agents: - It forms on reaction of higher strength acids with crude oil, this sludge blocks the pores.

Methods of Sludge prevention are-

- Solvent (Xylene, Toluene) preflush to minimize physical contact.
- Use of low strength acids.
- Non- ionic surfactants to minimize precipitation of colloidal suspension.

3. Corrosion inhibitors: -

A factors affecting corrosion during an acid treatment are-

- Temperature
- Contact time
- Acid concentration
- Metal type; and
- The corrosion inhibitor used.
- Degree of agitation.

Agitation increases the corrosion rate, at low levels of agitation corrosion rate decreases and at high levels corrosion rate increases, thus it is recommended that oxygen should be excluded from the test bubbling nitrogen through the acid solution.

Note: - In our case anti-sludge agent and iron controlling agent are not required due to iron control by pickling method and the tubing is new.

E) Afterflush: -

The precipitation of $Si(OH)_4$ may limit the success of sandstone acidization treatment. To minimize the impact of precipitation an afterflush is employed and the well be retained to production immediately. The afterflush to be used is diesel oil to ensure that the precipitation from the spent acid occurs away from the critical region near the wellbore. This afterflush also serves to dilute the acid thereby reducing the precipitation tendency.

Results and Recommendation: -

According to case study for acidization of sandstone, results are as follows:

Volume of Preflush per meter thickness of formation = 2.1 m^3

Rate of injection for acid treatment = 6.74 X 10^{-4} m^3/sec.

Volume of acid mixture required for acid treatment = 2.69 m^3

Treatment time = 66 minutes

Final productivity ratio (J_s/J_d) = 2.10

Concentration of acid mixture for acid treatment is 1.5 wt% HF and 12 wt% HCl.

As per the case study, given well is oil well thus diesel oil can be used as afterflush. It is desired to push the spent acid 3-4 feet away from the wellbore.

Recommendations: -

Recommendations for the matrix acidization are as follows-

- Coolants along with buffer is pumped immediately after Preflush to cool the near wellbore zone.
- If optimum injection rate is higher than maximum injection rate then acidization can be done at lower rate than maximum rate. As skin removed with time, optimum rate can be achieved.
- Proper anticipation against of formation due to deposition of scales (corrosion of tubing during execution) is must.it is possible by using Coil Tubing Unit.
- Transportation of acid (liquids) should be done in tanker which is coated with inert material internally to avoid corrosion.
- Fluoroboric acid is a good alternative for acidization of sandstone as it provide deep penetration.
- Strategic implementation and detail laboratory study is required, regarding selection of acids and additives. Additives and acids used must be compatible with formation fluid and formation rock to make job successful.

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