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Well Stimulation and Sand Production Management (PGE 489)

Acid Types and Reactions with Different Rocks

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What is Acidizing?

- Unsteady, non-isothermal, 3-D flow in porous media with chemical reactions
- Heterogeneous and homogeneous reactions
- Continuous variation in the porosity and permeability of the porous medium due to dissolution of the rock matrix and precipitation of the reaction products

Factors Affecting Acid Formula

- Damage type and location
- Rock mineralogy
- Analysis of formation water
- Bottom hole temperature
- Well completion
- Well type
- OWC Line

Factors Affecting Acid Formula

- Oil type (wax, asphaltenes)
- H_2S content
- Reservoir pressure
- Permeability profile
- Water saturation

Acids Types

- Mineral acids
- Simple organic acids
- Mineral/organic acids
- Powder or solid acids
- Chelating agents
- In-situ generated acids

Acids Types

- Mineral acids
  - Hydrochloric acid (HCl)
  - Sulfuric acid (H_2SO_4)
  - Phosphoric acid (H_3PO_4)
  - Nitric acid (HNO_3)

Acids Types

- Hydrochloric acid (HCl)
    - Cost effective
    - Available at 31 and 37 wt%
    - Ca, Mg chlorides are soluble
    - Fast reaction with calcite
    - Slower reaction with dolomite
    - Corrosive at high temp

Acids Types

- Hydrochloric acid (HCl)
  - Measure acid using titration
  - Colorless, slightly yellow/green
  - No impurities:
    - Iron
    - Sulfate
    - Phosphate
    - Fluoride

Acids Types

- Simple organic acids
    - More expensive
    - Mainly acetic and formic acids
    - Be careful with their salts
    - Less corrosive
    - With or without HCl
    - Reversible reactions
    - Requires especial corrosion inhibitors

Acids Types

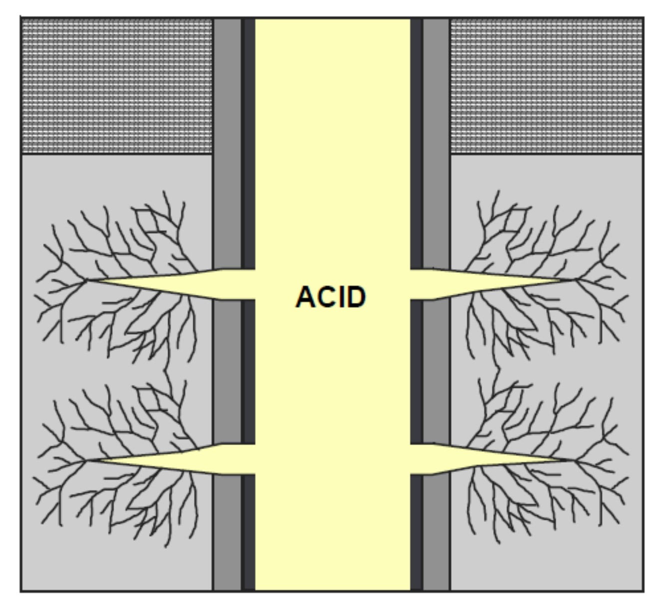
- Simple organic acids
  - Contains COOH
  - Acetic acid (CH_3COOH)
  - Formic acid (HCOOH)
  - Maximum concentration for acetic is 13 wt%
  - Maximum concentration for formic is 9 wt%
  - Mixture of HCl/organic acids
  - Mixture of formic/acetic

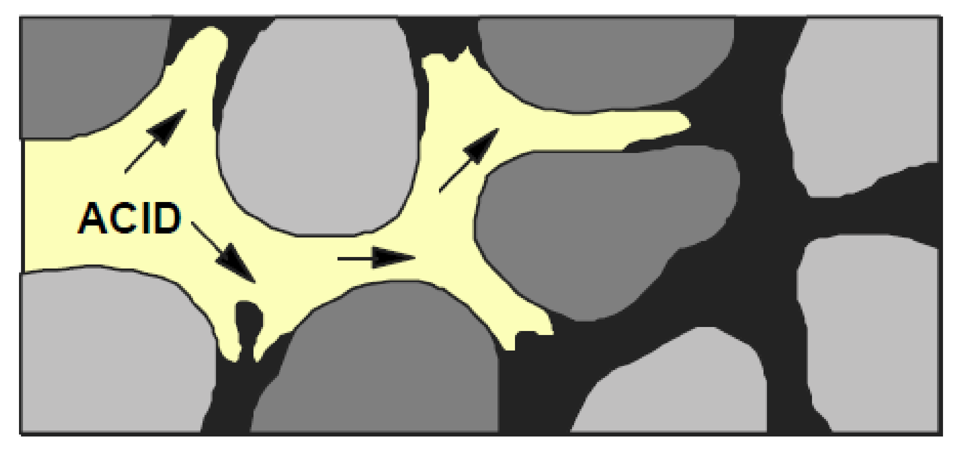
Matrix Acidizing

- Matrix acidizing design strongly depends on information about reservoir properties and formation damage.
- Acidizing process is complicated, and ***no model can describe the process precisely.***
- In many cases stimulation results deviate from what is expected from design.

Matrix Acidizing

- ***Matrix acidizing*** is a well stimulation technique in which an acid solution is injected into the formation in order to dissolve some of the minerals present, and hence, recover or increase permeability in the near-wellbore vicinity.
- Matrix Acidizing of **Carbonate** Reservoirs
- Matrix Acidizing of **Sandstone** Reservoirs



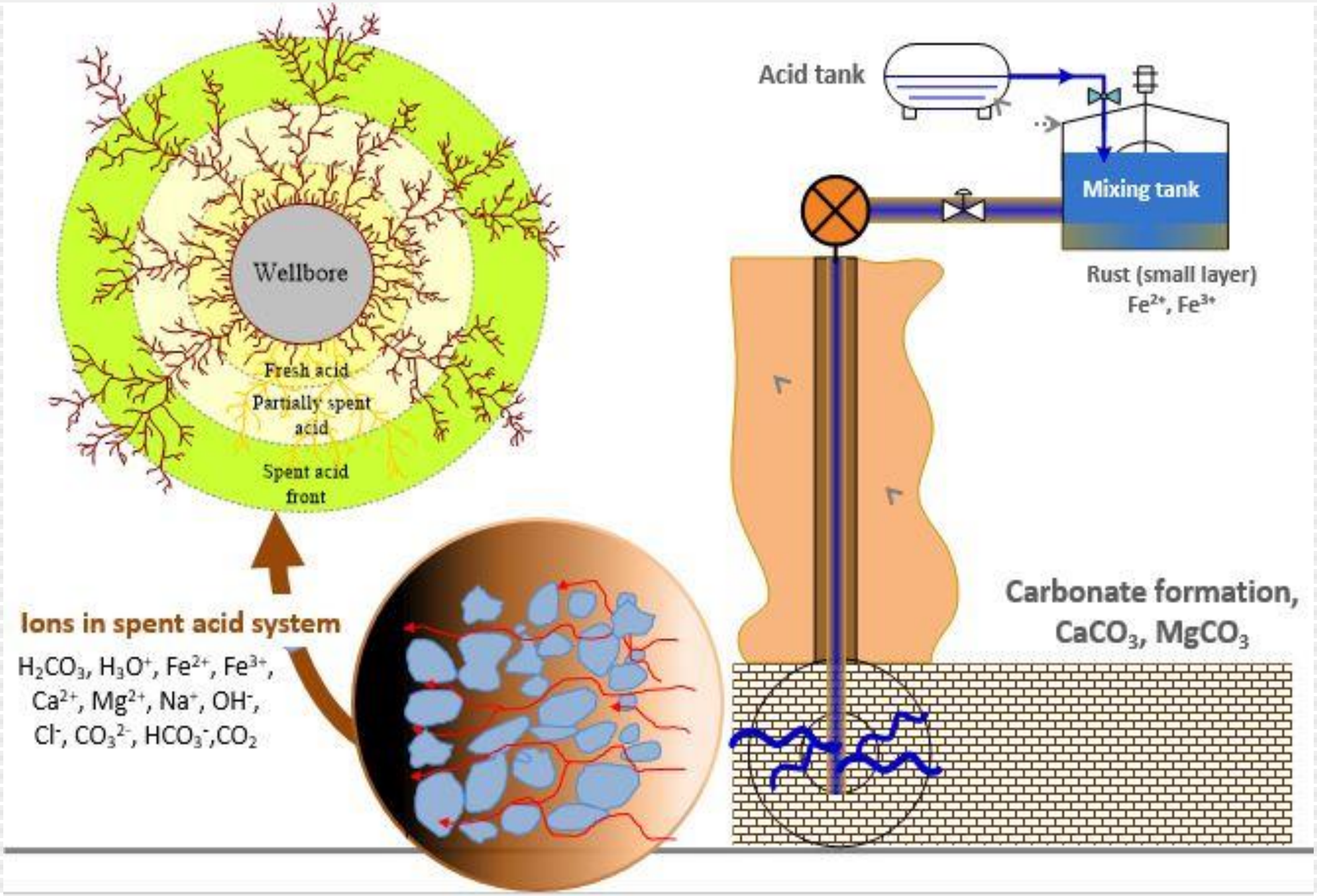


Matrix Acidizing

- The most common acids used in are hydrochloric acid (HCl), used to dissolve carbonate minerals, and mixture of hydrochloric and hydrofluoric acids (HCl/HF), for attacking silicate minerals such as clays and feldspars in Sandstone reservoir.

- Matrix acidizing is a near-wellbore treatment, with all of the acid reacting within about a **foot** of the wellbore in Sandstone formation, and within a few to perhaps **10 ft** of wellbore in Carbonate.

Matrix Acidizing



Matrix Acidizing

“*The lack of a method to determine the depth of damage penetration by existing methods of well test analysis continues to make the acidizing of oil wells an inexact science*”

J. L. Gidley (1970)

Matrix Acidizing

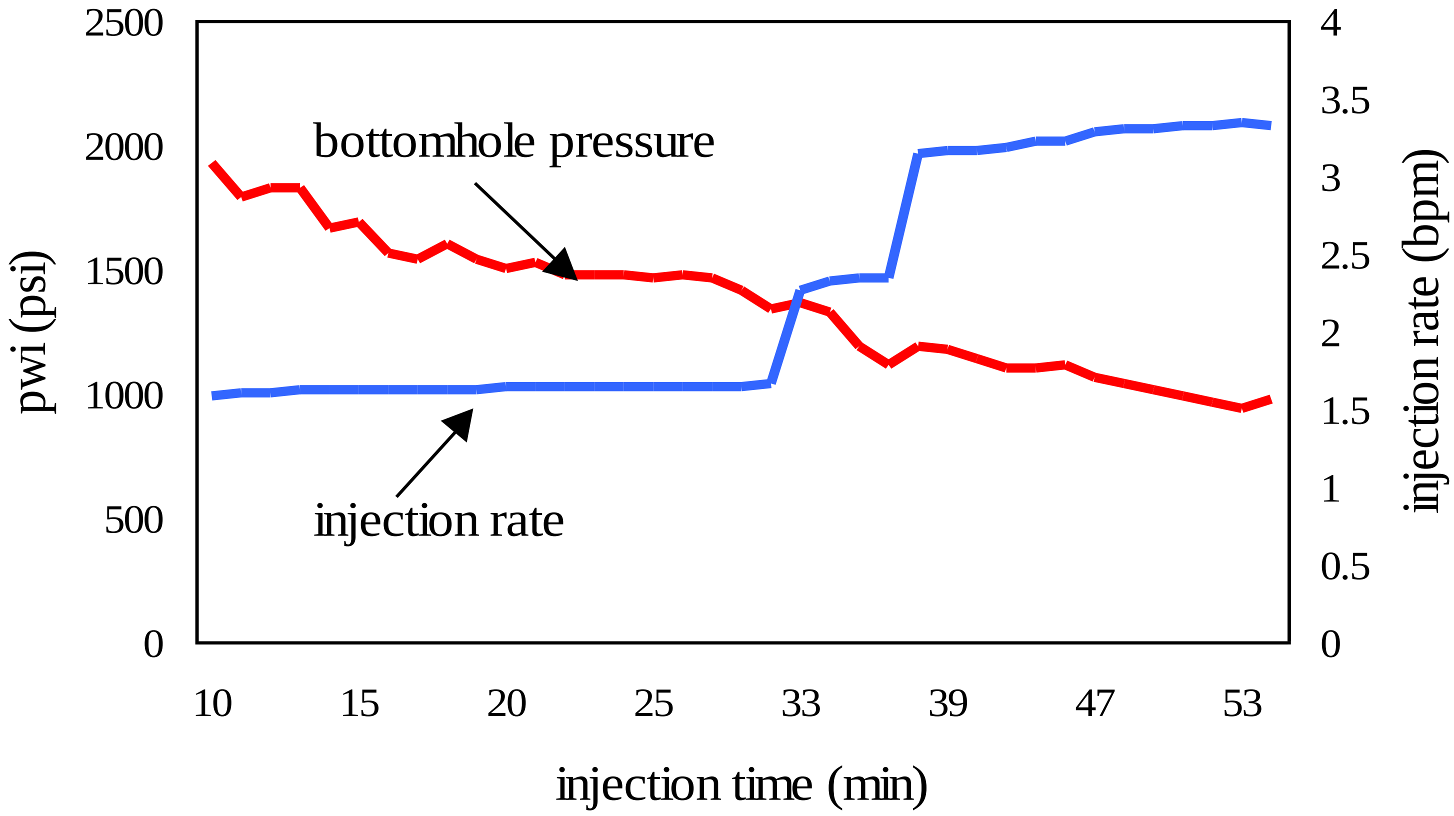
Q: What can we do to prevent “bad” acid treatments?

A: Monitor actual skin change during the injection.

- Evaluate acid systems
- Quantify damage removal
- Evaluate diversion process
- IMPROVE design for subsequent treatments

Field Examples

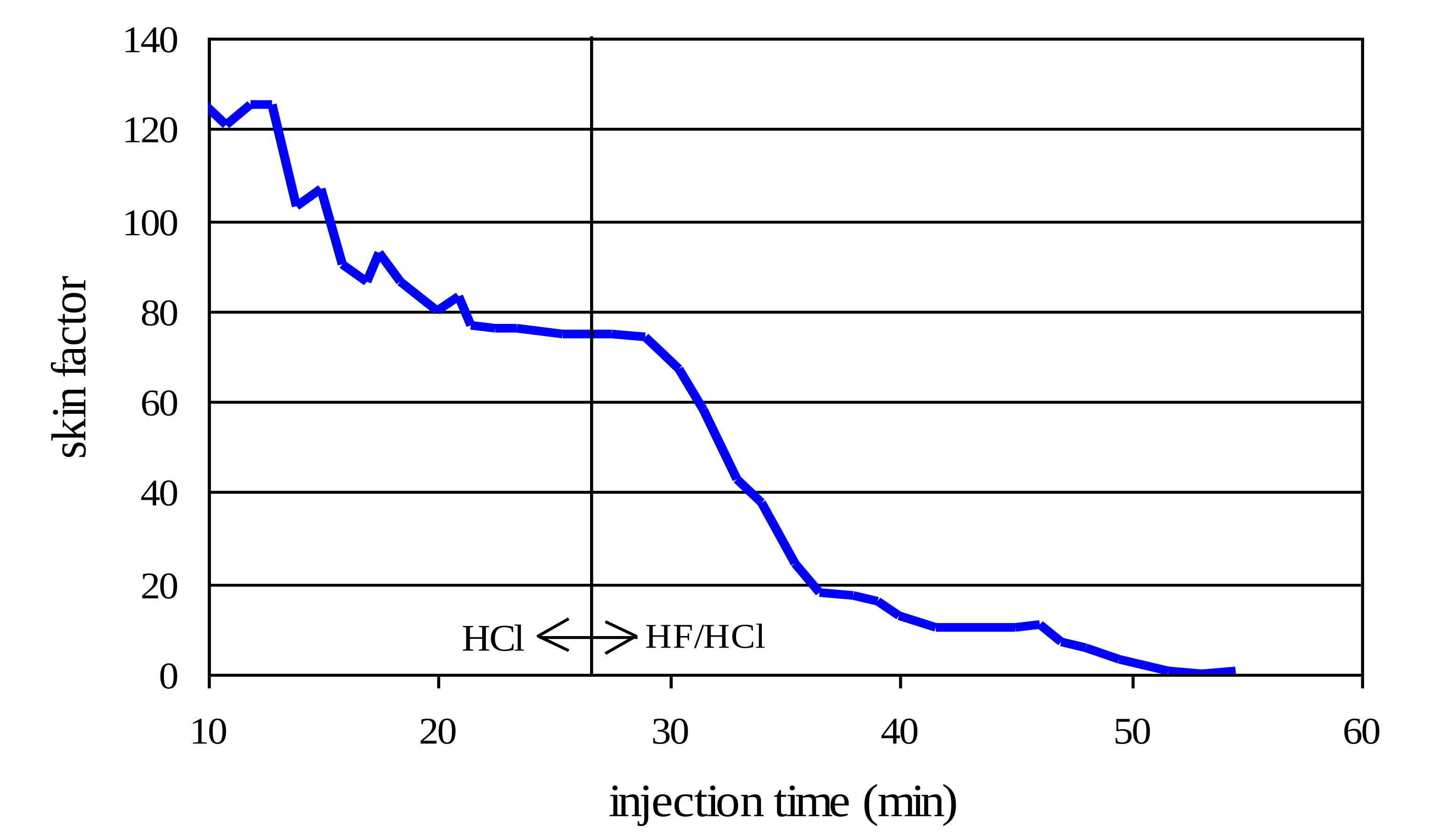
Example: Successful case *Pressure and injection rate record*



Field Examples

Example: Successful case

Skin Evolution of Acidizing



Field Study Examples

Example-1:

- Reservoir properties

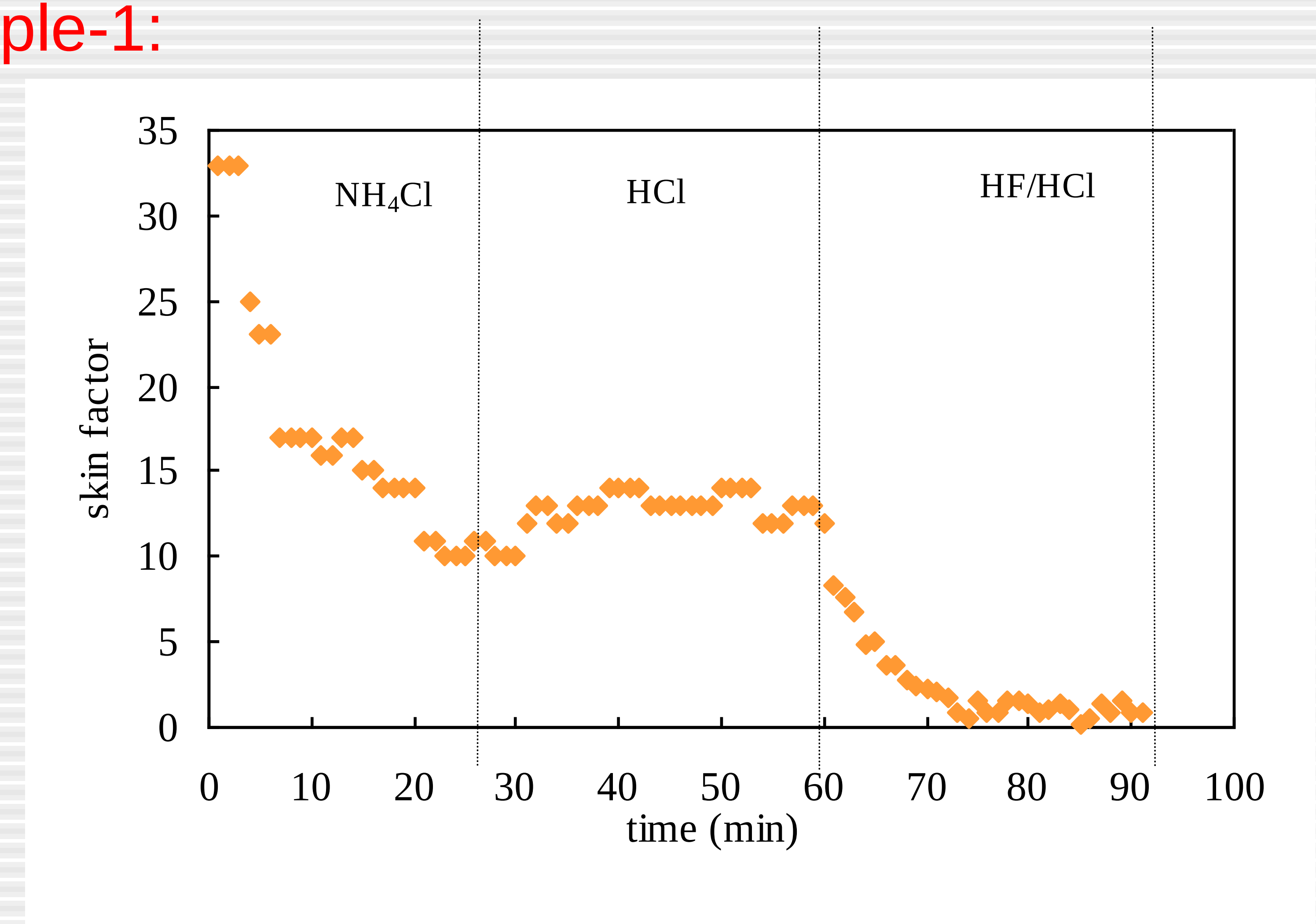
reservoir pressure	8000 psi
permeability	100 md
initial skin factor	35
payzone thickness	138 ft
well depth	11447 ft

- Treatment data

	No. stages	V (gal)
preflush	1	4957
main	1	9949
diversion	n/a	
spacer	2	5006

Field Study Examples

Example-1:



Field Study Examples

Example-1:

- Skin factor reduced from **35** to near zero
- Production was doubled and drawdown was reduced from 1200 psi to 500 psi by the treatment
- HCl did not remove the damage - common in sandstone formation with low carbonate

Field Study Examples

Example-2:

Reservoir properties

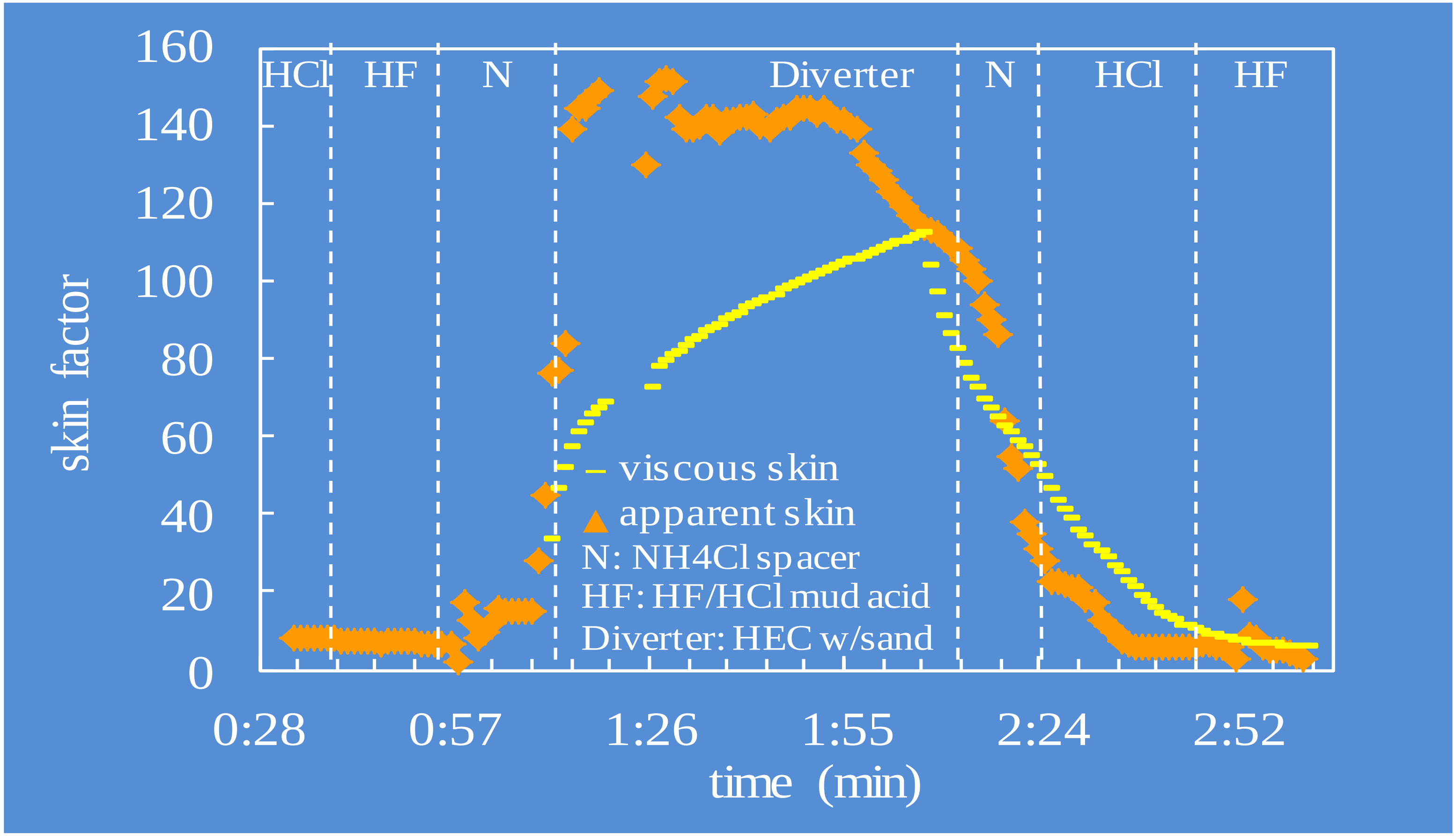
reservoir pressure	1700 psi
permeability	150 md
initial skin factor	8
payzone thickness	54 ft
well depth	3600 ft

Treatment data

	No. stages	V (gal)
preflush	2	2095
main	2	4199
diversion	1	407
spacer	3	4000

Field Study Examples

Example-2:



Field Study Examples

Example-2:

- The well did not respond as expected to the first acid injection
- Sudden increasing of skin factor when diverter reached the perfs showed positive diversion effect
- Two components of diversion effect on skin: filter cake build-up and viscous effect

Field Study Examples

Example-3:

- Reservoir properties

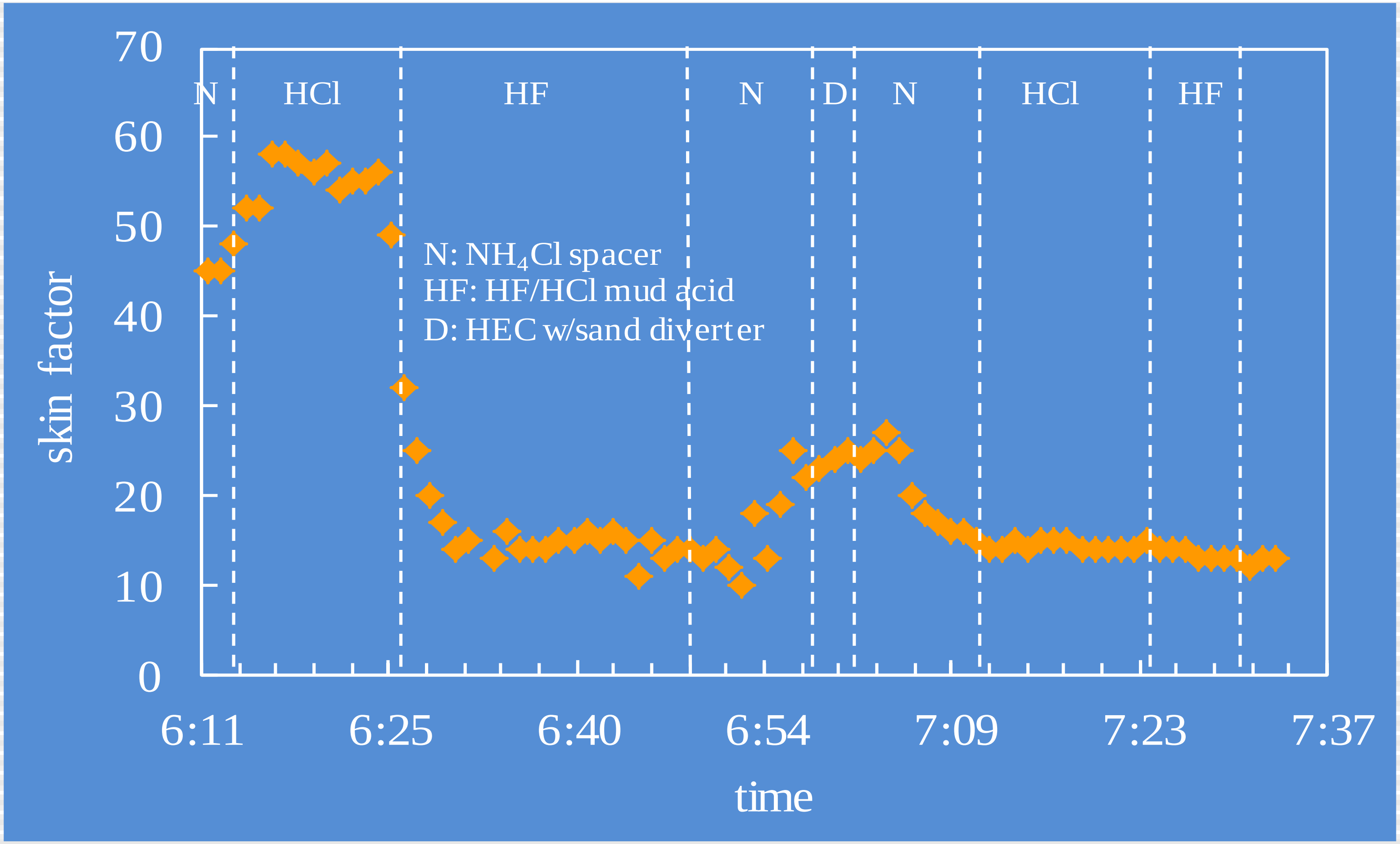
reservoir pressure	3100 psi
permeability	150 md
initial skin factor	45
payzone thickness	132 ft
well depth	7460 ft

- Treatment data

	No. stages	V (gal)
preflush	2	3444
main	2	7732
diversion	1	210
spacer	3	2289

Field Study Examples

Example-3:



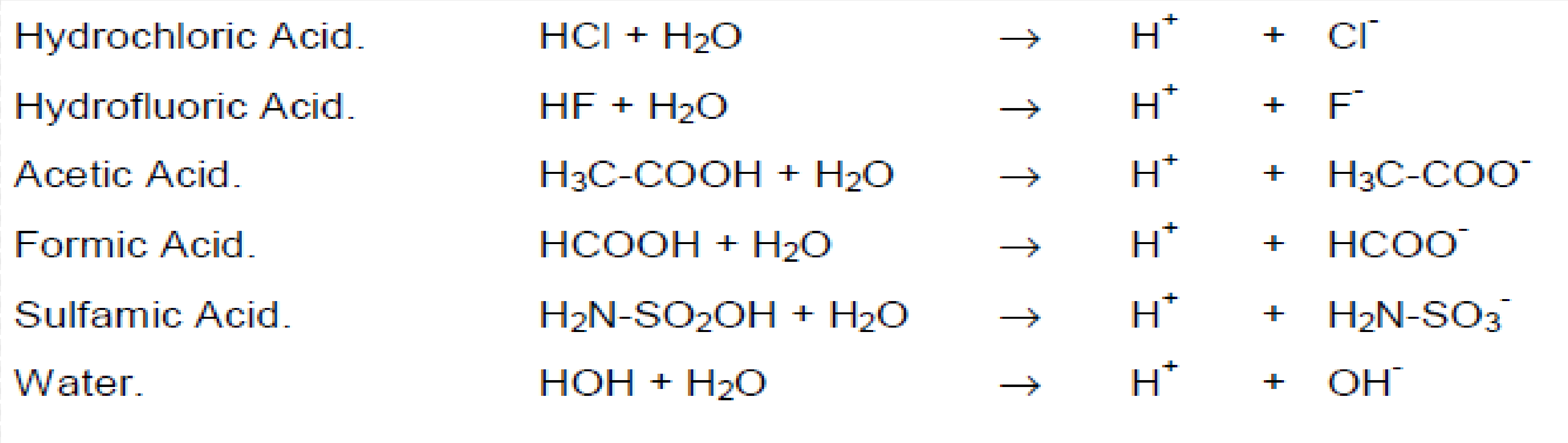
Field Study Examples

Example-3:

- Very successful stimulation in the first acid stage
- The second diversion stage could be eliminated since the second acid stage did not reduce skin factor any further

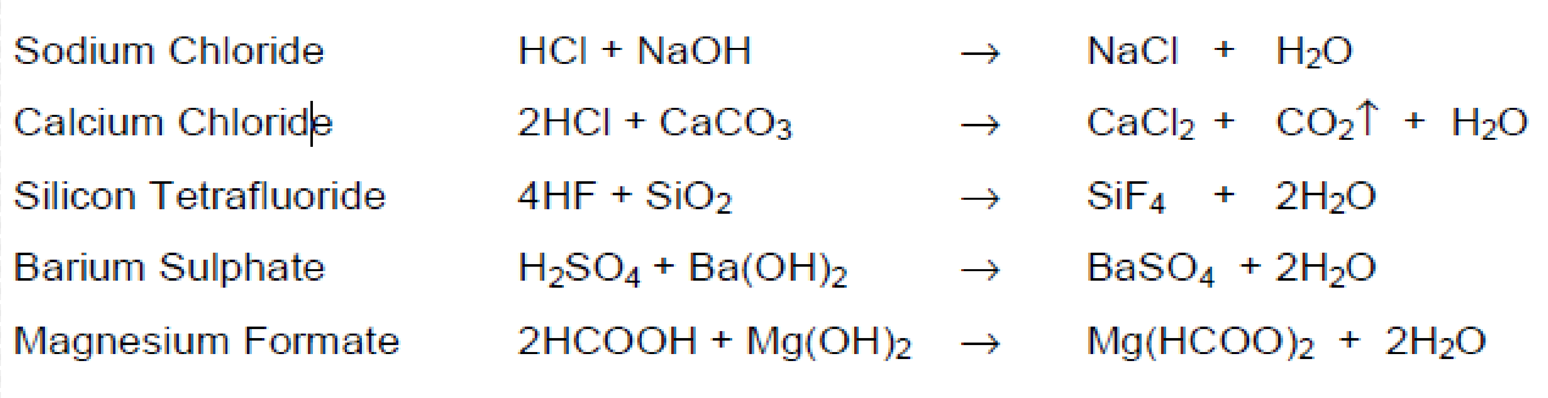
Fluid Chemistry

- An acid is a compound that when dissolved in (or hydrolysed by) water, it releases hydrogen ions (H+) as the cation. Examples of commonly used acids are as follows:



Hydrochloric Acid.	$HCl + H_2O$	→	H^+	+	Cl^-
Hydrofluoric Acid.	$HF + H_2O$	→	H^+	+	F^-
Acetic Acid.	$H_3C\text{-}COOH + H_2O$	→	H^+	+	$H_3C\text{-}COO^-$
Formic Acid.	$HCOOH + H_2O$	→	H^+	+	$HCOO^-$
Sulfamic Acid.	$H_2N\text{-}SO_2OH + H_2O$	→	H^+	+	$H_2N\text{-}SO_3^-$
Water.	$HOH + H_2O$	→	H^+	+	OH^-

- A salts is a compound formed by the reaction of an acid with a base.

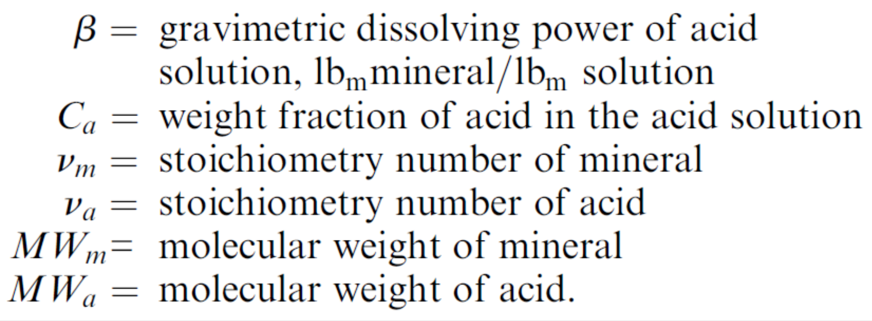


Sodium Chloride	$HCl + NaOH$	→	$NaCl$	+	H_2O		
Calcium Chloride	$2HCl + CaCO_3$	→	$CaCl_2$	+	$CO_2\uparrow$	+	H_2O
Silicon Tetrafluoride	$4HF + SiO_2$	→	SiF_4	+	$2H_2O$		
Barium Sulphate	$H_2SO_4 + Ba(OH)_2$	→	$BaSO_4$	+	$2H_2O$		
Magnesium Formate	$2HCOOH + Mg(OH)_2$	→	$Mg(HCOO)_2$	+	$2H_2O$		

Reaction Kinetics

- Dissolving power expresses the amount of minerals that can be consumed by given amount of acid on a mass or volume basis.

$$\beta = \frac{\nu_{\text{mineral}} MW_{\text{mineral}}}{\nu_{acid} MW_{acid}} = C_a \frac{\nu_m MW_m}{\nu_a MW_a}$$



β = gravimetric dissolving power of acid solution, lb_mmineral/lb_m solution

C_a = weight fraction of acid in the acid solution

ν_m = stoichiometry number of mineral

ν_a = stoichiometry number of acid

MW_m = molecular weight of mineral

MW_a = molecular weight of acid.

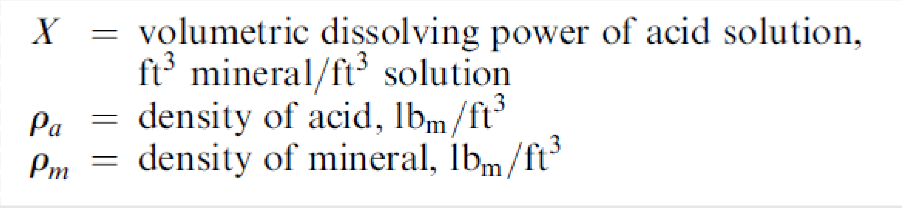
- For reaction between 100% HCl and $CaCO_3$:

$$\beta = \frac{\nu_{\text{mineral}} MW_{\text{mineral}}}{\nu_{acid} MW_{acid}} = \frac{(1)(100.1)}{(1)(36.5)} = 1.37 \frac{Ib_m\ CaCO_3}{Ib_m\ HCl}$$

Reaction Kinetics

- Volumetric Dissolving power (X) is defined as the volume of mineral dissolved by a given volume of acid, and related to gravimetric dissolving power by:

$$X = \beta \frac{\rho_{\text{acidsolution}}}{\rho_{\text{mineral}}} = \beta \frac{\rho_a}{\rho_m}$$



X = volumetric dissolving power of acid solution, ft^3 mineral/ft^3 solution

ρ_a = density of acid, lb$_m$/ft^3

ρ_m = density of mineral, lb$_m$/ft^3

- For reaction between 15% HCl and $CaCO_3$ with acid specific gravity of 1.07 and $CaCO_3$ density of 169 Ib$_m$/ft^3, the volumetric dissolving power is:

$$X = ((0.15)(1.37))\left(\frac{Ib_m\, CaCO_3}{Ib_m\, 15\%HCl}\right)\left(\frac{(1.07)(62.4)\, Ib_m\, 15\%\, HCl}{ft^3\, 15\%HCl}\,\Bigg|\,\frac{ft^3\, CaCO_3}{169\; IbmCaCO_3}\right)$$

$$X = 0.082\,\frac{ft^3\, CaCO_3}{ft^3\, 15\%HCl}$$

Reaction Kinetics

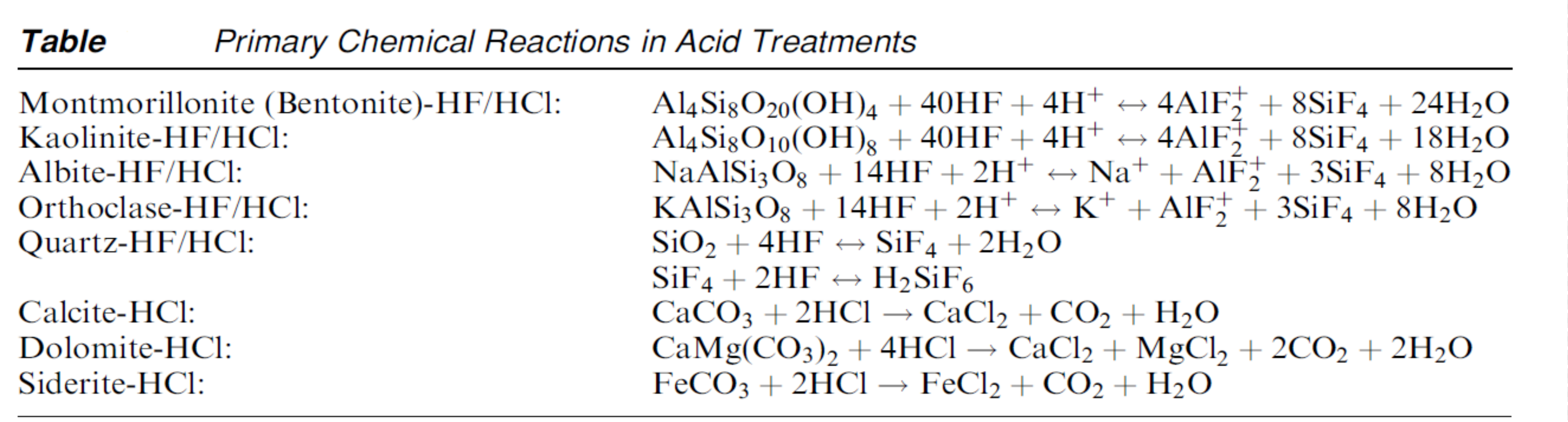


Table *Primary Chemical Reactions in Acid Treatments*

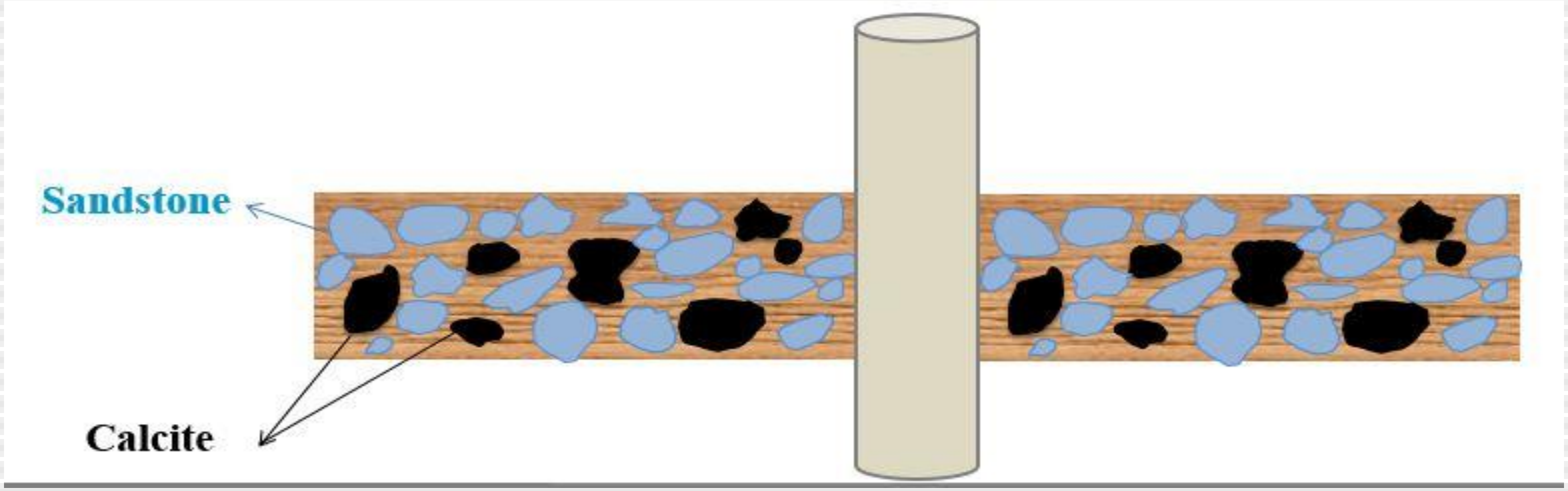
Montmorillonite (Bentonite)-HF/HCl:	$Al_4Si_8O_{20}(OH)_4 + 40HF + 4H^+ \leftrightarrow 4AlF_2^+ + 8SiF_4 + 24H_2O$
Kaolinite-HF/HCl:	$Al_4Si_8O_{10}(OH)_8 + 40HF + 4H^+ \leftrightarrow 4AlF_2^+ + 8SiF_4 + 18H_2O$
Albite-HF/HCl:	$NaAlSi_3O_8 + 14HF + 2H^+ \leftrightarrow Na^+ + AlF_2^+ + 3SiF_4 + 8H_2O$
Orthoclase-HF/HCl:	$KAlSi_3O_8 + 14HF + 2H^+ \leftrightarrow K^+ + AlF_2^+ + 3SiF_4 + 8H_2O$
Quartz-HF/HCl:	$SiO_2 + 4HF \leftrightarrow SiF_4 + 2H_2O$ $SiF_4 + 2HF \leftrightarrow H_2SiF_6$
Calcite-HCl:	$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$
Dolomite-HCl:	$CaMg(CO_3)_2 + 4HCl \rightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O$
Siderite-HCl:	$FeCO_3 + 2HCl \rightarrow FeCl_2 + CO_2 + H_2O$

Dissolving Power of Various Acids

Formulation	**Acid**	**β100**	**X**			
			5%	**10%**	**15%**	**30%**
Limestone $CaCO_3$ ρ=2.71 g/cm^3	HCl	1.37	0.026	0.053	0.082	0.175
	HCOOH	1.09	0.020	0.041	0.062	0.129
	CH3COOH	0.83	0.016	0.047	0.047	0.096
Dolomite $MgCa(CO_3)_2$ ρ=2.87 g/cm^3	HCl	1.27	0.023	0.031	0.071	0.152
	HCOOH	1.00	0.018	0.036	0.054	0.112
	CH3COOH	0.77	0.014	0.027	0.041	0.083

Matrix Acidizing - Example

In sand stone acidizing treatment, a preflush of HCl is usually injected ahead of the HF/HCl mixture to dissolve the carbonate minerals and establish a low-pH environment. A sandstone with a porosity of **0.20** containing **10%** (volume) calcite ($CaCO_3$) is to be acidized. If the HCl preflush is to remove all carbonate to a distance of **1 ft** from the wellbore before HF/HCl stage enters the formation, what is the minimum preflush volume is required in gallons of acid solution per foot of formation thinness? The wellbore radius is **0.328 ft**.



Matrix Acidizing - Solution

The required minimum acid volume to dissolve all calcite is:

$V_{acid}=V_{pore}+V_{\text{to dissolve CaCO3}}+V_{replaceCaCO3}$

The volume of acid needed to react with calcite (V_m/X)

$$V_m = \pi(r_{HCl}^2 - r_w^2)(1-\phi)x_{CaCO_3}$$

$$V_m = \pi(1.328^2 - 0.328^2)(1-0.20)(0.1) = 0.42\ ft^3/ft\ CaCO_3$$

$$\frac{V_m}{X} = \frac{0.42}{0.082} = 5.01\ ft^3\ HCl/ft$$

The volume of pore space within 1 ft of wellbore is:

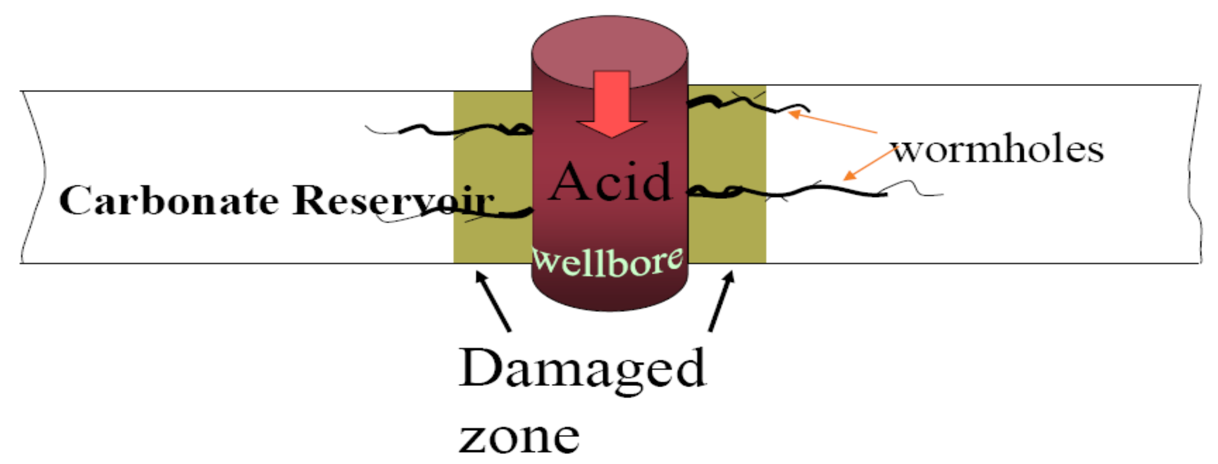
$$V_p = \pi(r_{HCl}^2 - r_w^2)\phi$$

$$V_p = \pi(1.328^2 - 0.328^2)(0.1) = 0.52\ ft^3/ft$$

$$V_{HCl} = \frac{V_m}{X} + V_p + V_m = \frac{(5.01+0.52+0.42)\,ft^3}{ft}\,\Bigg|\,\frac{7.48\,gal}{ft^3} = 44.5\,gal/ft$$

Wormhole Modeling

- Acids were used to create wormholes to connect the formation to the wellbore
- Propagation of wormholes through the damaged zone yields negative skin
- Only a small fraction of the matrix must be dissolved



Wormhole Modeling

- A few large channels called wormholes form
- Structure of wormholes depends on many factors including:
    - Flow geometry
    - Injection rate
    - Reaction kinetics
    - Mass transfer rates

Wormhole Modeling

- Much larger than pores, hence insignificant pressure drop through them
- If the wormholes propagate through the damaged zone,

$$S = -\ln(r_{wh}/r_w)$$

- Ex: 1.7 foot long wormholes propagating from a 6 inch radius well yield Skin of -1.22
- Wormhole structure depends on rock type, acid type, injection rate, temperature, …

Wormhole Modeling

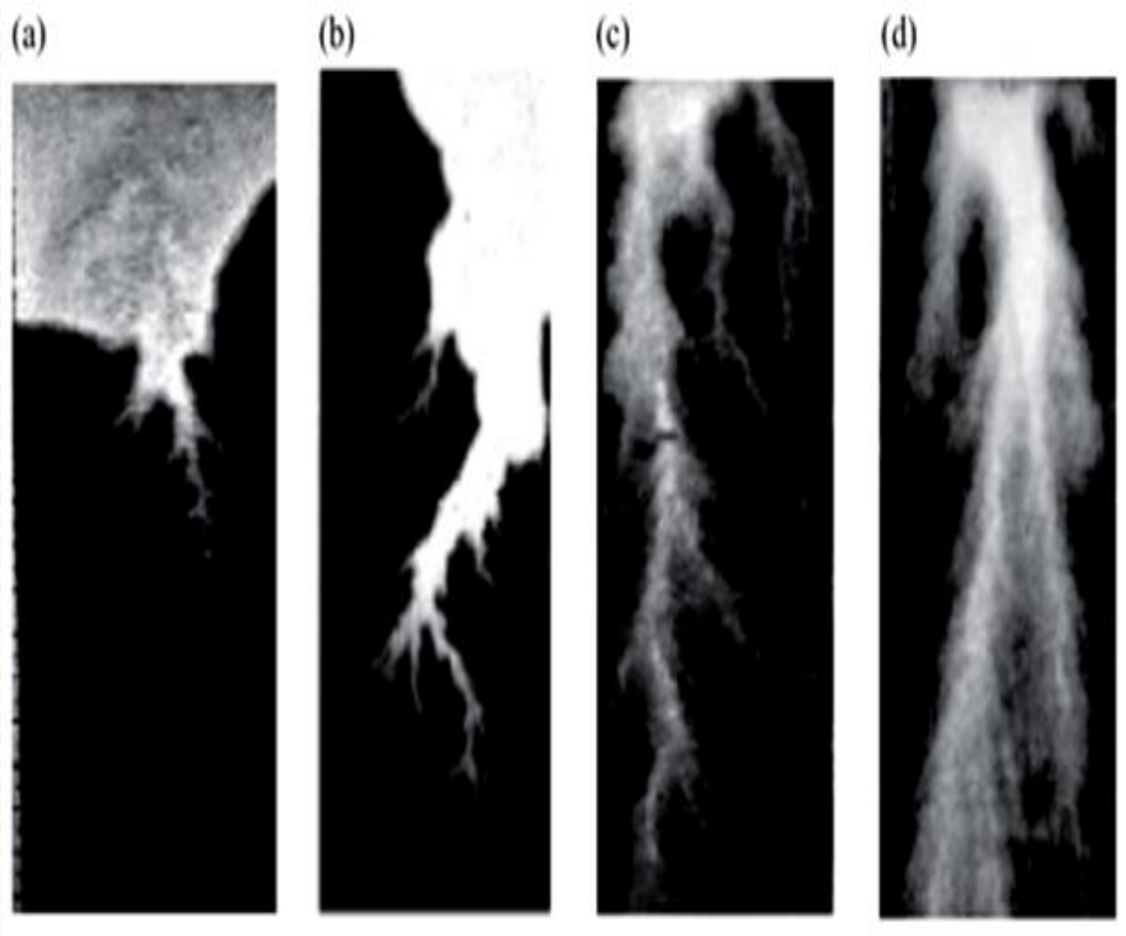
- Objective of acid stimulation was to create sufficiently long wormholes to give a post-treatment negative skin factor of –2 to –3.
- Injection rate may be limited by coiled tubing size
- Low injection rate resulted in compact dissolution of the formation face with no significant wormhole penetration
- The analysis can show that the skin factor did not change significantly throughout the entire treatment

Wormhole Modeling

- Acid selection based on:
  - reservoir depth (shallow or deep)
  - reservoir fracture gradient
  - reservoir permeability
  - Heterogeneity

Optimum Wormhole Condition

Dissolution Patterns in Carbonate Acidizing



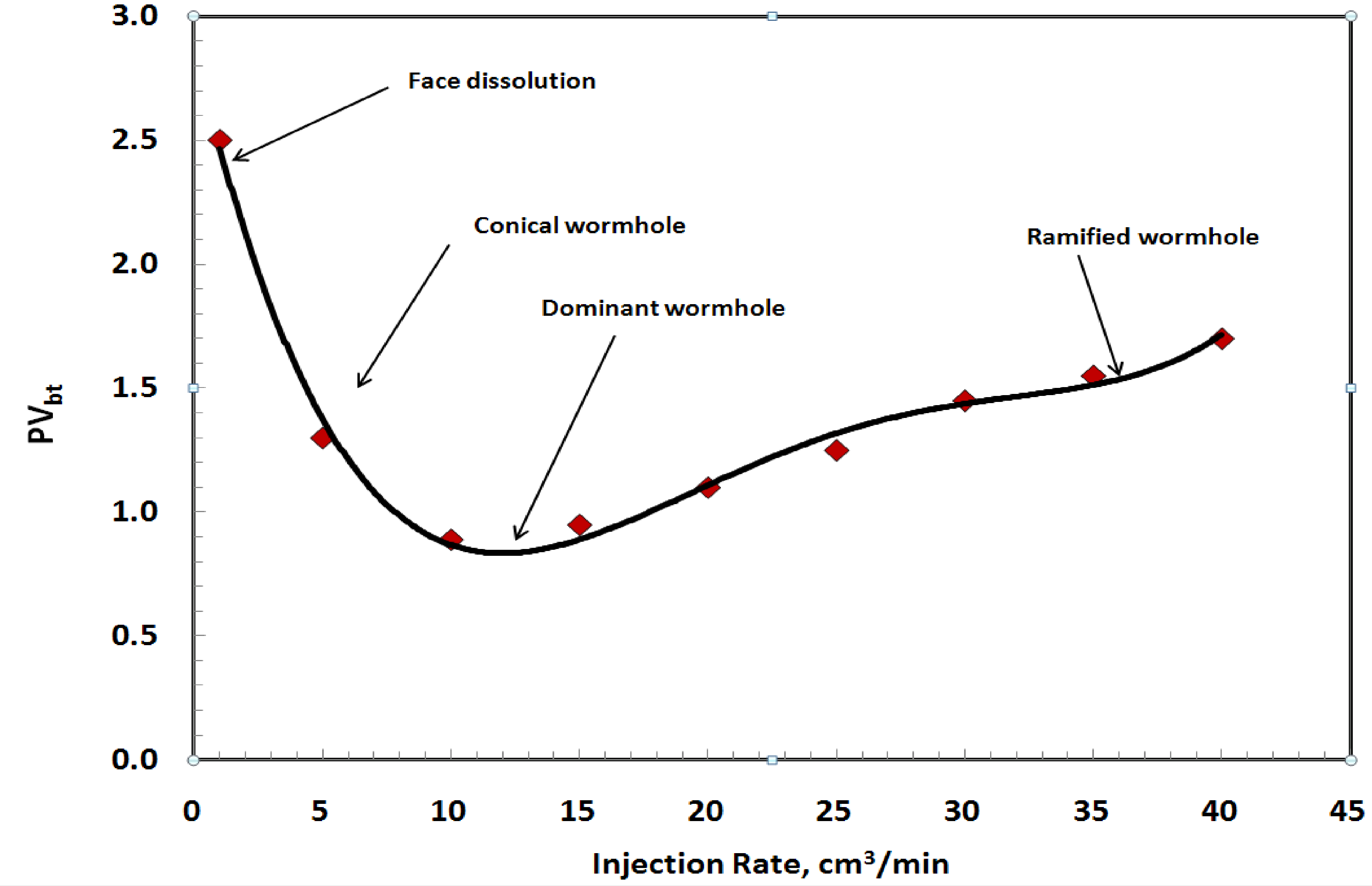
a. 0.1 cc/min, face dissolution

b. 0.2 cc/min, conical

c. 1 cc/min, dominant

d. 4.1 cc/min, ramified

Optimum Wormhole Condition



Optimum Wormhole Characterization

Dissolving Power:

Gravimetric (β)

$$\beta = \frac{MW_{CaCO_3} \cdot \alpha_{CaCO_3}}{MW_{acid} \cdot \alpha_{acid}}$$

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

$\beta_{100\%}$ = 100.1 * 1/(36.5 *2) = 1.37 lbmole $CaCO_3$/lbmole HCl

Optimum Wormhole Characterization

Volumetric dissolving Power (X)

$$X = \beta \frac{\rho_{acid}}{\rho_{CaCO_3}}$$ **ft³ CaCO₃/ft³ HClc**

$$V_{acid} = V_{CaCO_3} / X$$

$$V_{CaCO_3} = \pi \left(r_{acid}^2 - r_w^2 \right) \left(1 - \phi \right) x_{CaCO_3}$$ **ft³ CaCO₃/ft**

Optimum Wormhole Characterization

Acid Capacity Number (N_{ac}):is the ratio of the amount of mineral dissolved by the acid occupying a unit volume of the rock pore space to the amount of mineral present in the unit volume of the rock

$$N_{ac,acid} = \frac{\phi\, \beta_{\%}\, \rho_{acid}}{(1-\phi)\rho_{rock}} = \frac{\phi\, X}{(1-\phi)}$$

Optimum Wormhole Characterization

Damköhler Number (N_{Da}): the ratio of reaction rate to convection rate

$$N_{Da} = \frac{\pi d_w L_w \kappa}{q}$$

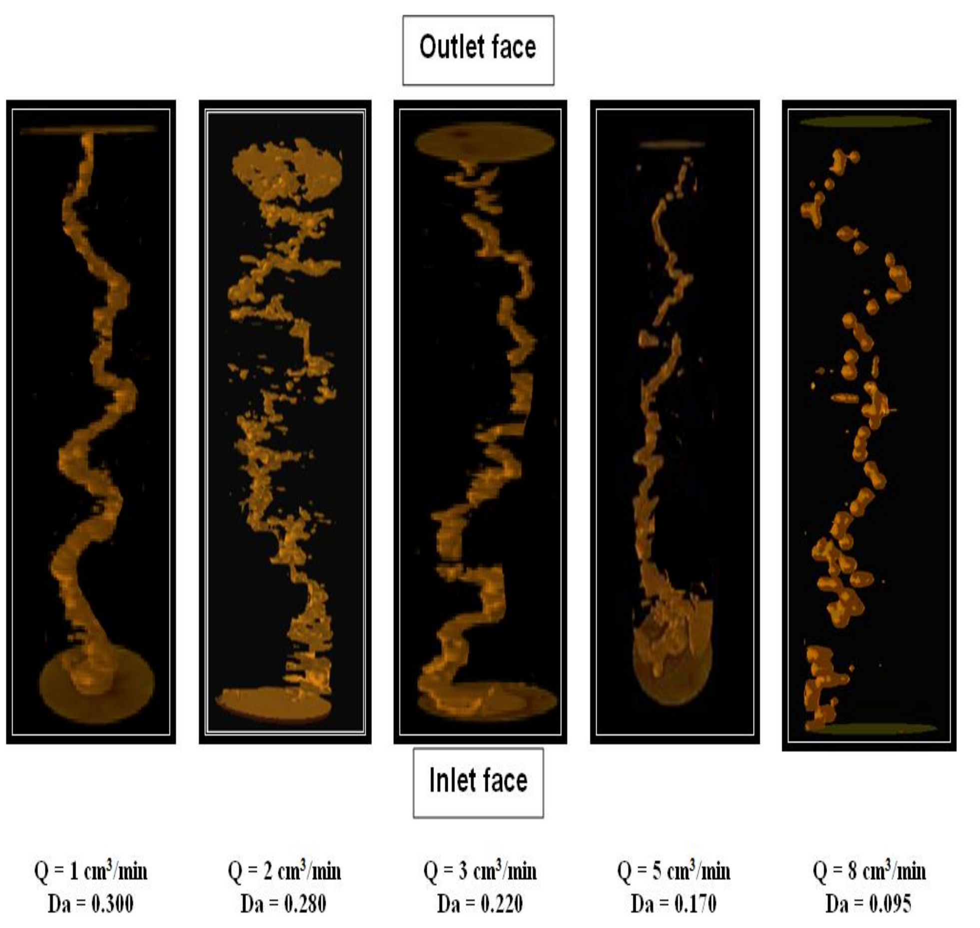
d_w = wormhole radius, cm

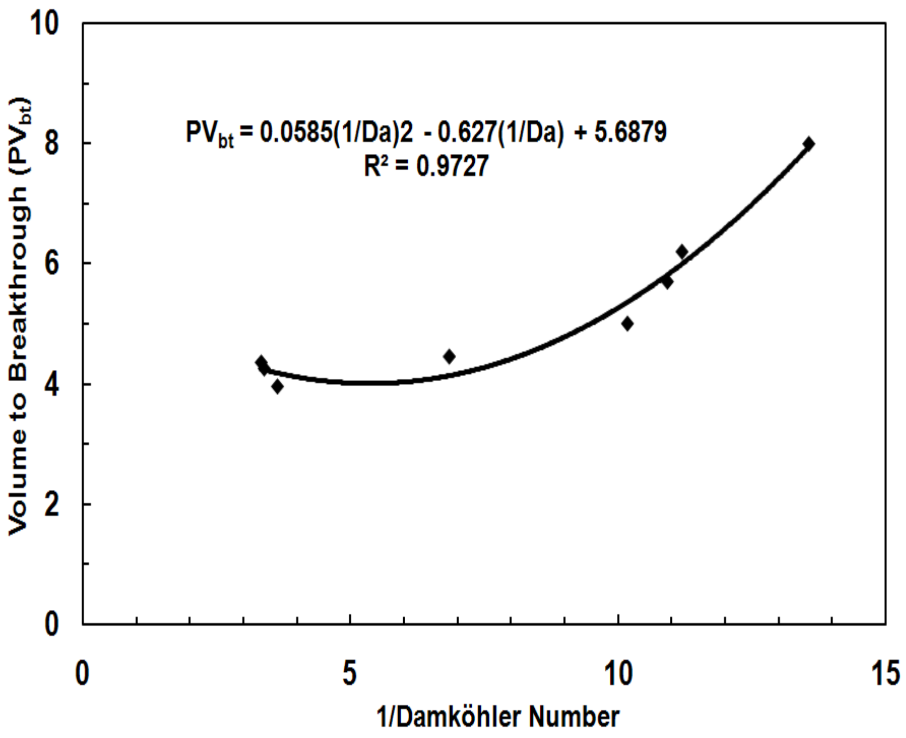
L_w = wormhole length, cm

k = overall dissolution rate constant, cm/s

q = injection rate, cm^3/s

Optimum Wormhole Characterization





Mahmoud and Nasr-El-Din, 2010, SPE 133497

Optimum Wormhole Characterization

The optimum Damköhler number was found to be **0.29**, we can design the treatment based on that number

In the case of irreversible reactions (mass transfer):

$$\kappa = \frac{1.86 D_e^{2/3}}{d_w} \left(\frac{4q}{\pi L_w} \right)^{1/3}$$

Optimum Wormhole Characterization

Using these equations, the optimum flux can be estimated:

$$u_{opt} = \frac{130 L_w D_e}{d_{core}^2}$$

u_{opt}= optimum flux, cm/s

L_w = wormhole length, cm

D_e = diffusion coefficient, cm^2/s

d_{core} = core diameter, cm

Optimum Wormhole Characterization

From the previous equation the optimum injection rate can be determined:

$$Q_{opt} = 47.1 d_{core}^{2} u_{opt}$$

Q_{opt} = optimum injection rate, cm^3/min

d_{core} = core diameter, cm

u_{opt} = optimum flux, cm/s

Optimum Wormhole Characterization

To scale up the optimum injection rate to the field conditions the following equation can be used:

$$Q_{well} = Q_{core} \frac{r_{well} h_f}{r_{core} L_{core}}$$

Q_{well} = optimum injection rate in the field,
Q_{core} = optimum injection rate in the coreflood,
r_{well} = well radius,
h_f = reservoir thickness,
r_{core} = core radius,
L_{core} = core length

Wormhole Penetration Radius

Different models can be used to predict for the wormhole radius:

$$r_{wh} = \left[\frac{bN_{ac}V}{\pi h \phi} D_e^{-2/3} \left(\frac{q}{h} \right)^{-1/3} \right]^{0.63}$$

Daccord et al., 1989

r_{wh} = wormhole penetration radius
b = constant = 1.5×10^{-5} in SI,
N_{ac} = acid capacity number,
V = q * t,
D_e = diffusion coefficient,
h = formation thickness,
ϕ = formation porosity,

Wormhole Penetration Radius

To determine the volume of the acid per foot thickness of the formation the following formula can be used:

$$\frac{V}{h} = \frac{\pi \phi D_e^{2/3} \left(\frac{q}{h} \right)^{1/3} r_{wh}^{1.6}}{b N_{ac}}$$

Wormhole Penetration Radius

Volumetric Model (Hill 1993):

- Assumes acid dissolves a constant fraction of rock volume penetrated
- Wormhole velocity is constant
- Assume fixed number of PV required to create a wormhole to a given distance

$$r_{wh} = \sqrt{r_w^2 + \frac{V}{\pi \phi h PV_{bt}}}$$

$$\frac{V}{h} = \pi \phi \left(r_{wh}^2 - r_w^2 \right) PV_{bt}$$

Wormhole Penetration Radius

Example:

Determine V/h (gal/ft) using different models for the following acid treatment:

- 15 wt% HCl, ρ_{acid} = 1.072 g/cc
- Well radius = 6 in.
- Wormhole penetration = 3 ft
- Injection rate = 0.1 bpm/ft
- Diffusion coefficient = 10^{-9} m^2/s
- Optimum flux = 0.18 cm/min
- Pore volume to breakthrough = 1.3 PV

Wormhole Penetration Radius

Solution:

$$N_{ac,acid} = \frac{\phi\,\beta_{\%}\,\rho_{acid}}{(1-\phi)\rho_{rock}} = 0.02$$

$$\frac{V}{h} = \frac{\pi\phi D_e^{2/3}\left(\dfrac{q}{h}\right)^{1/3} r_{wh}^{1.6}}{bN_{ac}} = 17.2\ gal/\ ft$$ Daccord

$$\frac{V}{h} = \pi\phi\left(r_{wh}^2 - r_w^2\right)PV_{bt} = 76.6\,gal/\ ft$$ Volumetric

Wormholing Rate

Buijse Model:

$$V_{wh} = W_{eff} v_i^{2/3}\left(1 - e^{\left(-W_b v_i^2\right)}\right)$$

$$v_i = \frac{q}{2\pi r h \phi}$$

$$v_{i-opt} = \frac{q_{opt}}{2\pi r h \phi}$$

$$w_{eff} = \frac{v_{i-opt}^{1/3}}{PV_{bt-opt}}$$

$$w_b = \frac{4}{v_{i-opt}^{2}}$$

Wormholing Rate

Huang et al.(1989)

$$v_{wh} = v_{i,tip}\left(\frac{C_{tip}}{C_0}\right)N_{Ac}$$

$$v_{i,tip} = \frac{q}{2\pi\phi h r_{wh}}$$

Mahmoud and Nasr-El-Din (2011)

$$v_{wh} = \frac{4Q\,N_{ac}}{\pi\phi d_{core} d_{wh}}$$

Wormholing Rate

Wormholing rate can be used to determine the volume of the fluid required to create wormholes

$$PV_{bt} = \frac{v_i}{v_{wh}}$$

Buijse 2005

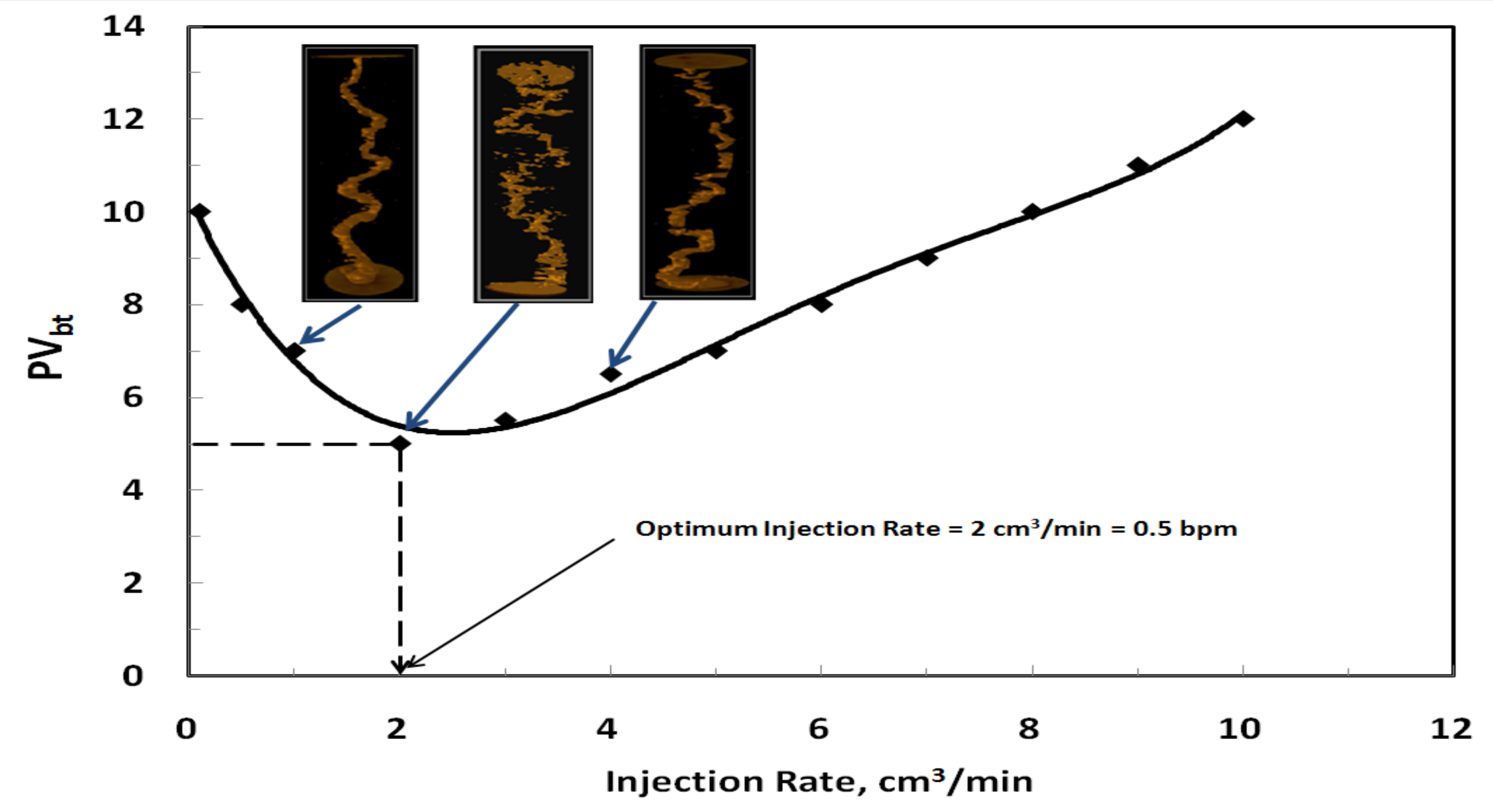
$$PV_{bt} = \frac{d_{wh}}{d_{core} N_{ac}}$$

Mahmoud and Nasr-El-Din, 2011

Then the PV_{bt} can be used to determine the acid volume required for the treatment by the volumetric model

Optimum Injection Rate

Optimum injection rate in acid treatment is the rate at which the dominant wormhole will be formed with the minimum acid volume



Optimum Injection Rate

Optimum injection rate cannot be used in certain situations

$$Q_{\max} = \frac{2\pi hk\left(g_{fr} D_r - p_r\right)}{\mu\left(\ln \frac{r_e}{r_w} + S\right)}$$

- Steady State Flow
- Open Hole
- Vertical Well

Q_{max} = maximum possible injection rate
h = reservoir thickness
k = reservoir permeability
g_{fr} = fracture gradient
D_r = reservoir depth
p_r = reservoir pressure
μ = fluid viscosity
r_e = reservoir drainage radius
r_w = wellbore radius
S = damage skin

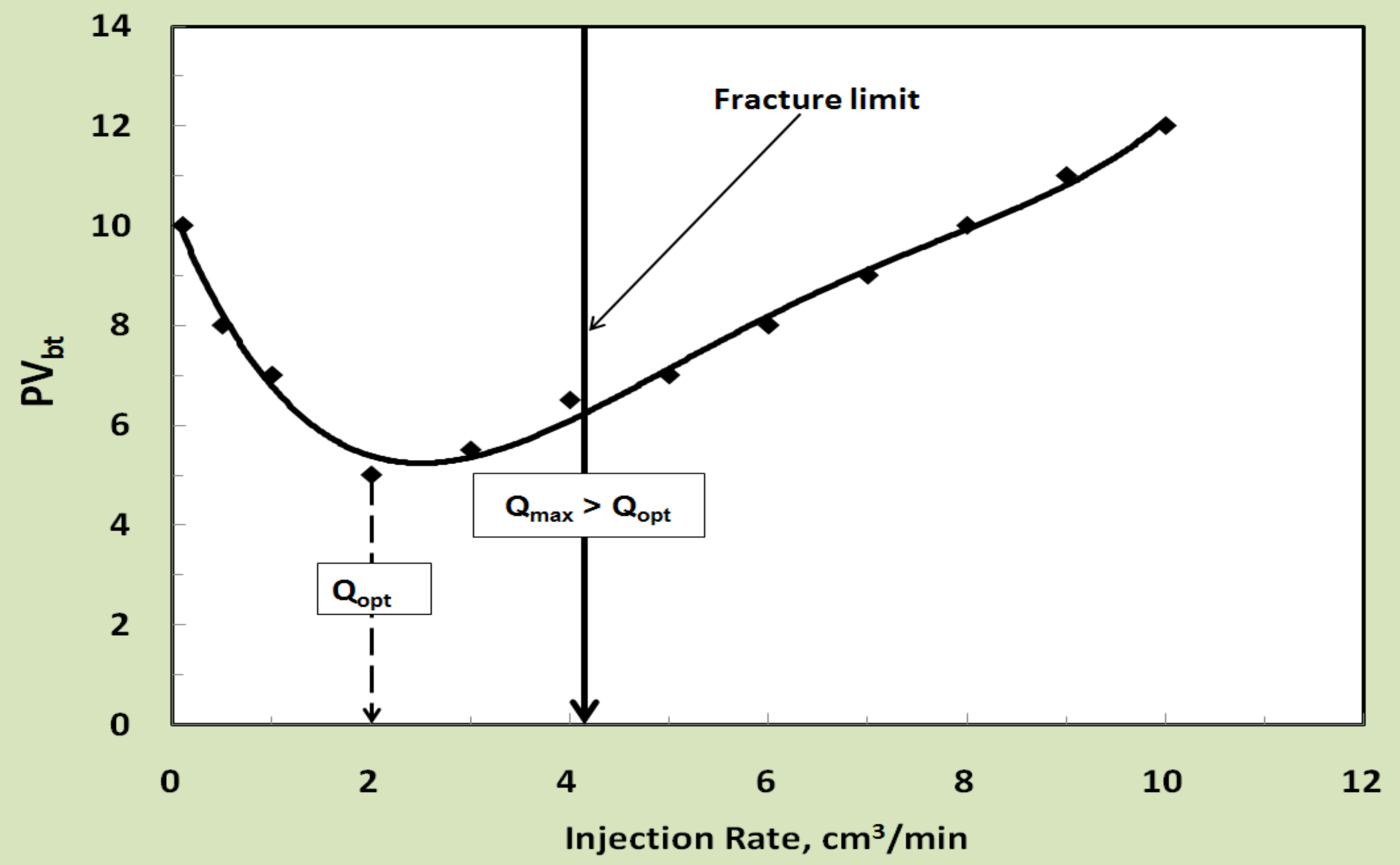
Optimum Injection Rate

The maximum injection rate can be determined according to the reservoir and completion type

- Steady state, pseudo steady state, or transient flow
- Open hole, perforate, or slotted liner
- Vertical, inclined, or horizontal well

Optimum Injection Rate

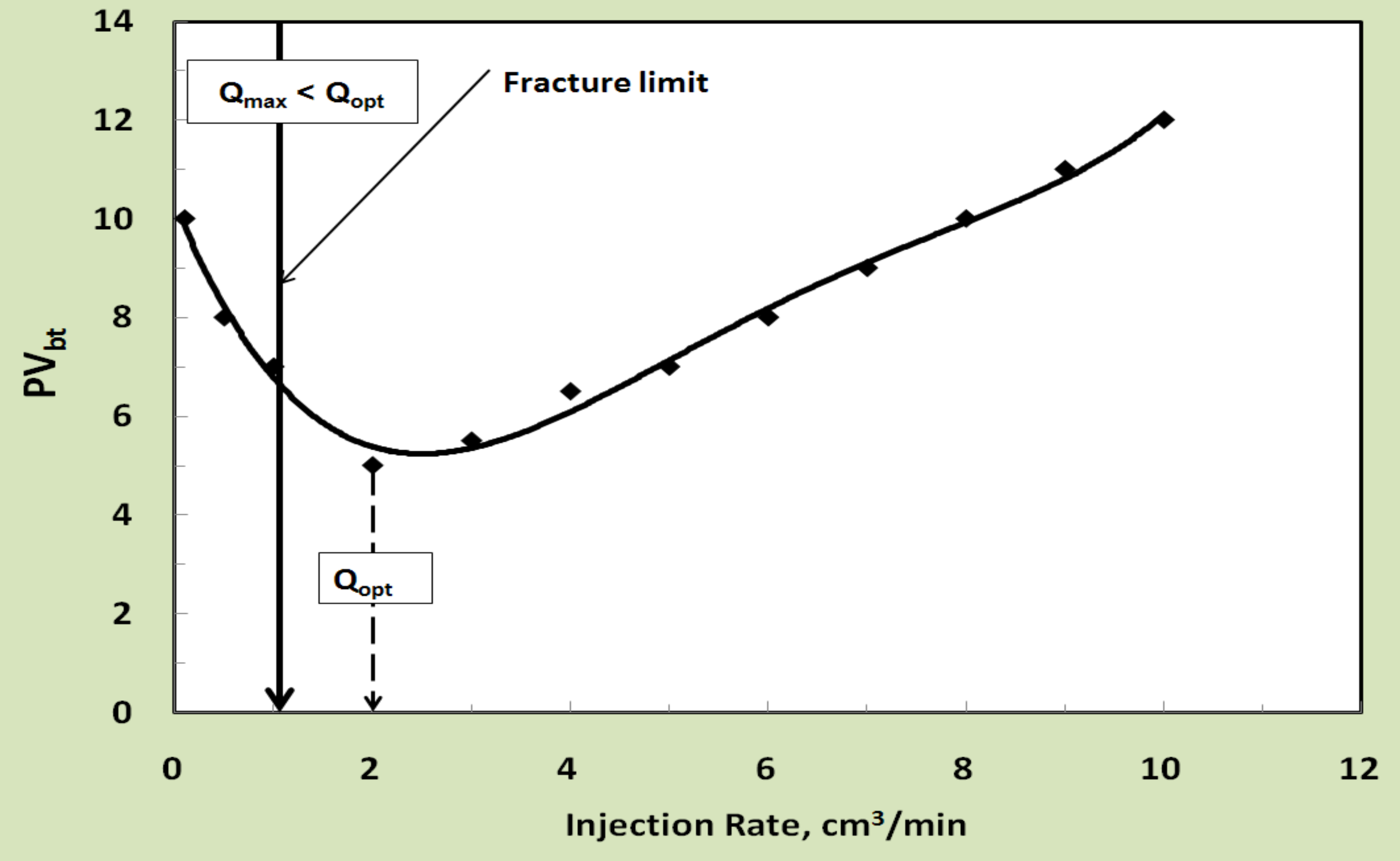
Scenario 1: $Q_{opt} < Q_{max}$, current stimulation fluid is safe to be used without the fear to frac the formation



This is good in deep reservoirs, but take care of the tubular corrosion

Optimum Injection Rate

Scenario 2: $Q_{opt} > Q_{max}$, current stimulation fluid is not safe, we have to look for alternatives



This situation is common in shallow reservoirs where the fracture pressure is low