Acid Diverting

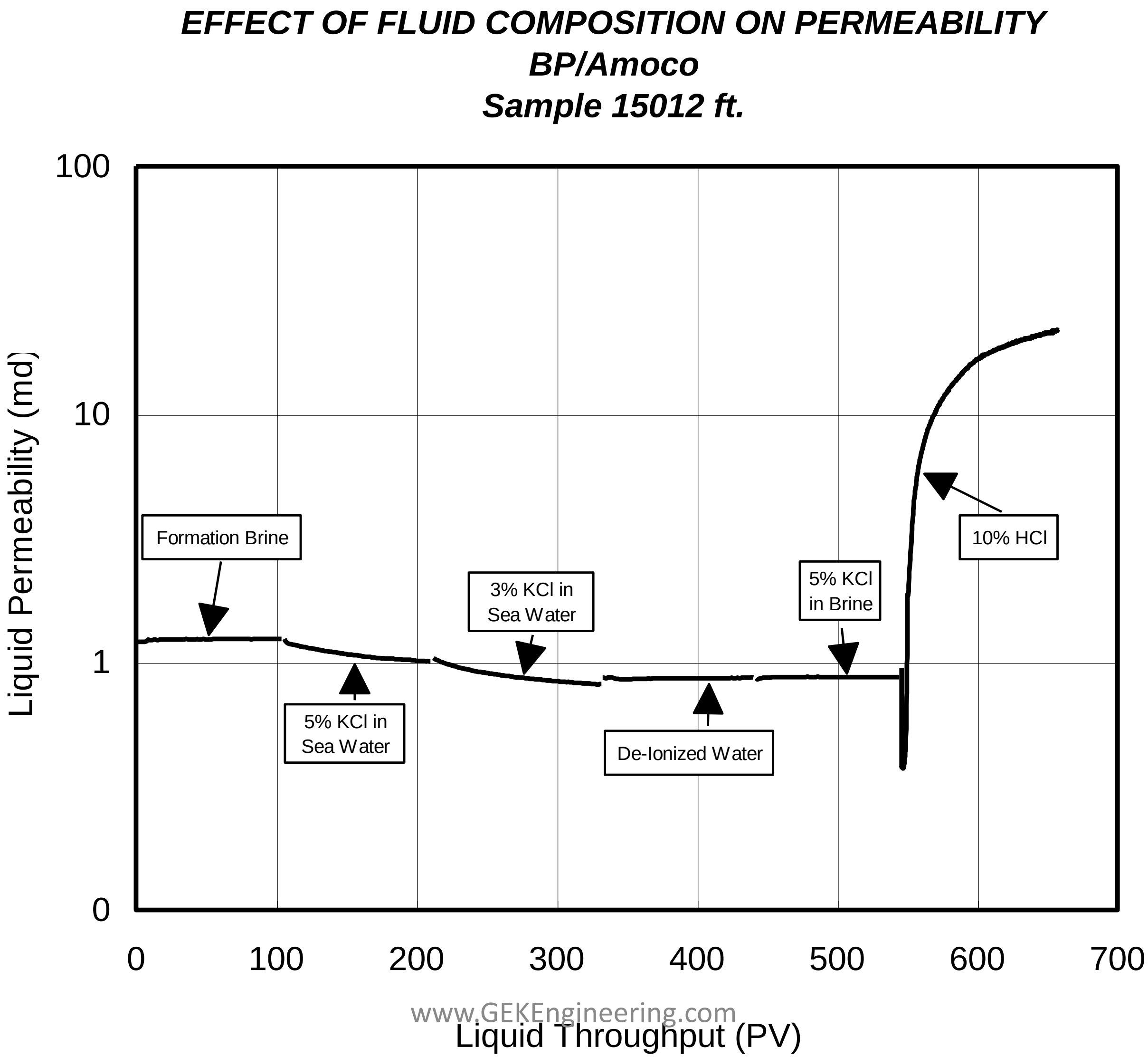
- Best use is usually damage removal in the connection from the reservoir to the wellbore.
- Limits
  - Acids follow the path of least resistance – go down the high permeability zones.

Acidizing

- Reasons
- Acid Types
- Reactions
- Methods

- Acidizing is a set of stimulation methods that are commonly used for damage removal and some permeability improvement.

Fluid Susceptibility Test on Core



Acids

- Acids used in well stimulation and cleanup
- The purpose of an acid is to remove formation damage or improve initial permeability.
- Look at the acid and the alternatives to the acid:
  - HCl, HCl/HF, acetic, formic
  - Solvents and surfactants, gasses,
  - Reperforating, explosives, under-reaming, surging,

Acids

- HCl - hydrochloric
- HCl/HF – hydrochloric and hydrofluoric mixture, often called mud acid.
- Acetic – most common use is vinegar (4%)
- Formic – ant and bee sting irritant.
- Others – sulfamic and chloroacetic are the dry acids or stick acids used for spot application of weak acids.

HCl or Hydrochloric (Muratic) Acid

Hydrogen chloride gas dissolved in water

- Maximum concentration about 36 to 38%, depending on temperature.
- HCl content lowers solubility to other gases and to salts.
- Common Concentrations
  - **5 to 10% washes for scale, pickling, and preflushes**
  - **10 to 15% for matrix acidizing**
  - **20 to 28% for fracturing**

HCl acid in Oil Industry (reasons for concentrations)

- 15% HCl, highest concentration of HCl that earliest inhibitor would work in.
- 28% HCl, highest concentration of HCl that can be hauled in an unlined steel tank (US highway regulation).

Best approach is to select what is needed for a specific application.

HCl Acid Byproducts

- calcium chloride salt (dissolved)
- CO_2 gas

Other common byproducts

- Emulsions, sludges, foams
- solids from nonreactive parts of formation

Acid Density

Acid	Initial	Spent
10% HCl	8.75 ppg	9 ppg
15% HCl	8.95 ppg	10 ppg
28% HCl	9.3 ppg	11 ppg

HCl/HF acids

- For use in removing clay and mud damage
- Don't use it on carbonates (yields a precipitate, calcium fluoride, CaF_2)
- Normal concentration is about 9% HCl and 1% HF.

HCl/HF concentrations

- 12% HCl / 3% HF - mud removal in wellbore
- 6% HCl / 1.5% HF - low clay content sandstones
- 9% HCl / 1% HF - moderate clay content sandstones

- The amount of HCl is increased to offset the spending on certain minerals such as aluminum in clays. The HF requires live HCl to prevent precipitation of HF reaction products.
- In most instances, the use of 12% HCl and 3% HF is not recommended for matrix acidizing (injection into the matrix).

Other Acids:

Phosphoric (rare) – not recommended in formations

- precipitates calcium phosphate when it spends on calcium minerals – inhibitors won't prevent it in the rock (inhibitors adsorb).
- low corrosion at high temp, but watch long term contact

Other Acids:

Sulfamic: (stick or solid acid)

- Use at BH temps below 150^o F – higher temperature may create sulfuric acid
- OK on light scales
- very limited dissolving power
- usually used without an inhibitor

Other Acids

Chloroacetic: (one of the powdered acids, also available in stick form)

- very limited reactivity
- low dissolving capacity
- effective at lowering pH and slowly removing some reactive scales.
- usually used without an inhibitor

Other Acids:

Citric:

- iron sequestering agent
- very limited reactivity

Other Acids:

Acetic

- limited reactivity
- limited iron control – can aggregate the formation of some sludges! Use with a sludge preventer.
- expensive for carbonate amount dissolved
- less corrosive at high temperatures
- maximum concentration used downhole is 10% (by-product solubility problems).
- Note: acetic is often used as the acid of choice at higher temperatures but has very limited reactivity and dissolving capacity (vinegar is 4% acetic).

Other Acids:

Formic:

- expensive for amount of carbonate dissolved (5 times HCl cost on a pound of carbonate dissolved basis)
- less corrosion than HCl at high temperature? Some evidence says no.

Acid Mixtures:

Acetic/ HCl

Formic/ HCl

- Advertised as “slower reacting” – but not not so much at higher temperatures
- iron control – pH type control only – watch sludge development. (Iron reducer control and an anti sludge surfactant are more effective at preventing sludges.)
- high temperature uses based on perception of less corrosion – tests are suggested for temperatures over 300F.

Other Acids

Formic/ HF

- high temperature sandstones – this is a useful product with few problem areas.
- less corrosion? - still needs inhibitor

Sulfuric and Nitric Acids

- Sulfuric acids not used because of insoluble sulfate by products with calcium. Sulfuric also reacts with and modifies some oils to sludges.
- Nitric acids not used because of danger of explosion. Also, no inhibitors.

Problems

- use of too strong an acid for damage
- use of too much acid
- wrong type of acid
- use of acid at all!
- Watch:
  - temp
  - reactants
  - time

Acid Reaction Basics

- Controls (Limits) on live acid penetration:
  - Matrix treating: area to volume ratio. In the matrix, the area to volume ratio is about 20,000:1 – this means the acid spends quickly if the formation or damage is acid soluble.
  - Fracture acidizing – with area-to-volume ratios of about 50:1, acid reaction is slower and the dominant control on penetration distance is leakoff into side pores and channels.

Acid Reaction, HCl-on- Carbonate

- Reaction type = first order (fast)

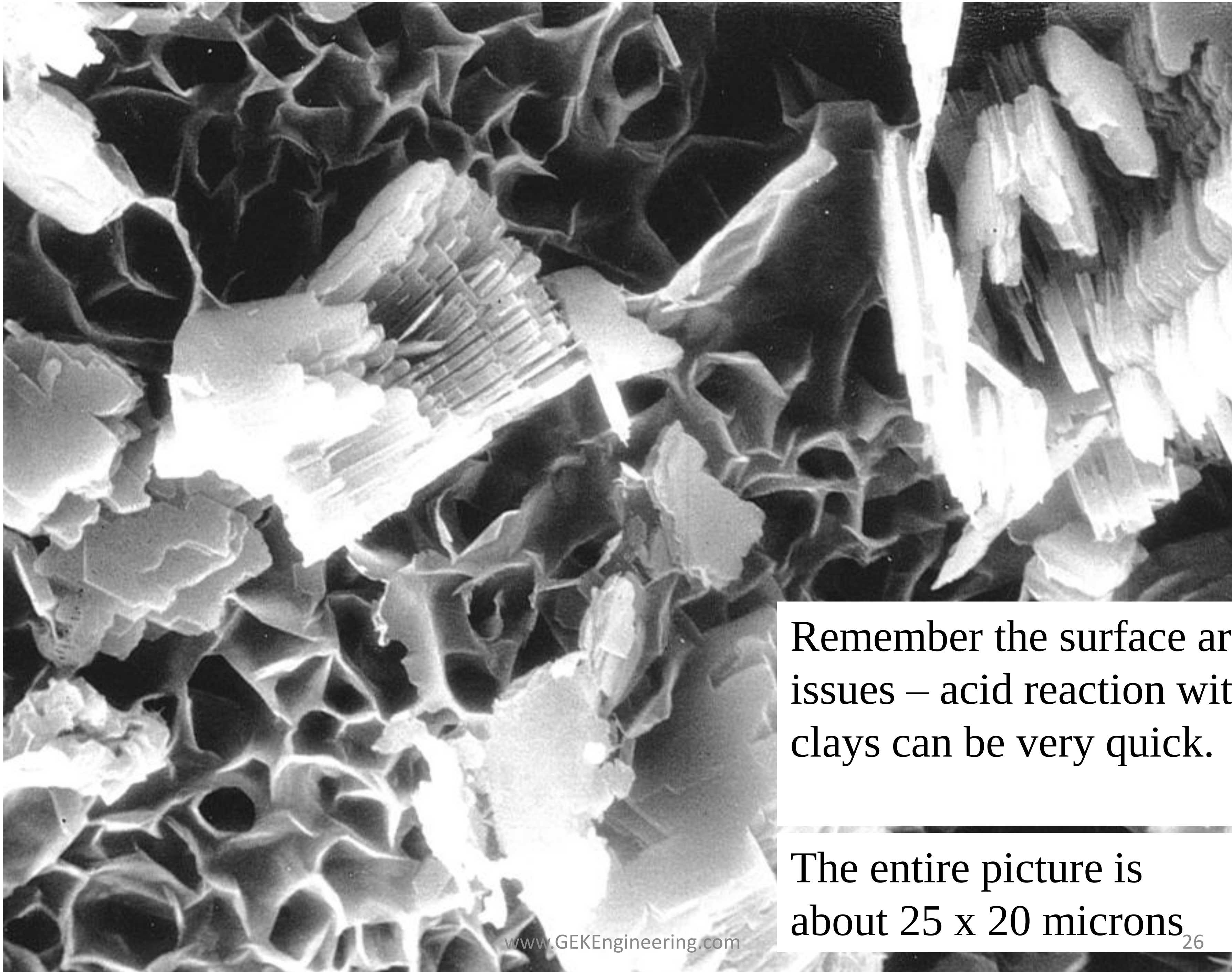
This means that acid spends as quickly as the acid reaches the formation surface and the byproducts are carried away.

Remember, the area-to-volume ratio controls the surface area presented to the acid for reaction. It also controls how much acid is there to react.

Area-to-Volume Ratio

- in wide (0.3”) fracture = 50:1
- in narrow (0.01”) fracture = 500:1
- in matrix (10% porosity) = 20,000:1


Natural Fracture in Limestone



Remember the surface area issues – acid reaction with clays can be very quick.

The entire picture is about 25 x 20 microns

Acid Reaction, HCl-on-Silica

- very, very slow

More of a tiny solubility of silica in acid than a reaction. Sand grains are very large compared to the reactive surface area of clays.

Area of Clays

Sand Grain	0.000015 m2/g
Kaolinite	22
Smectite	82
Illite	113
Chlorite	60

The areas for clay are highly variable and depends on deposit configuration. However, the difference between authogenic clay area and sand grain area are on the order of 6 to 7 orders of magnitude.

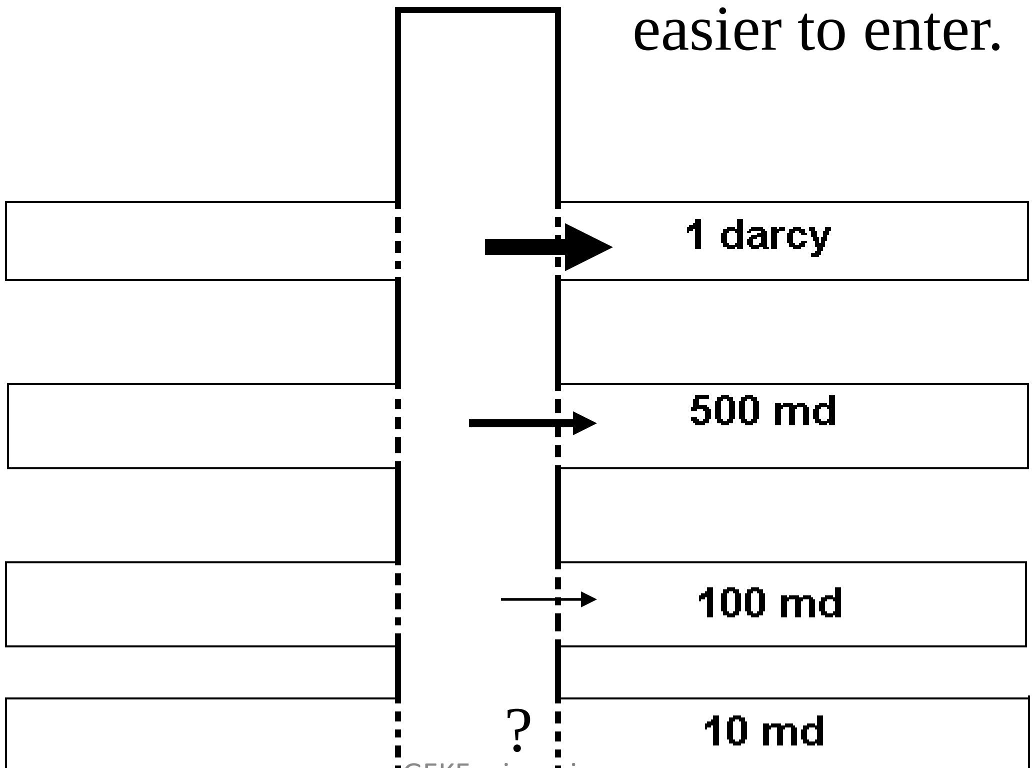
Second Acid Penetration Control - Leakoff

- Leakoff is required to get acid to flow into the zone. Without it there is no reaction.
- However! By reacting with the flow path, acid increases the rate of leakoff, making injection into other zones much less likely.

Diverting

Without any modification of the flow path, where will most of the acid go?
=> Along the path of least resistance.

How do you treat the other zones? => Make the high permeability zones harder to enter or the low perm zones easier to enter.

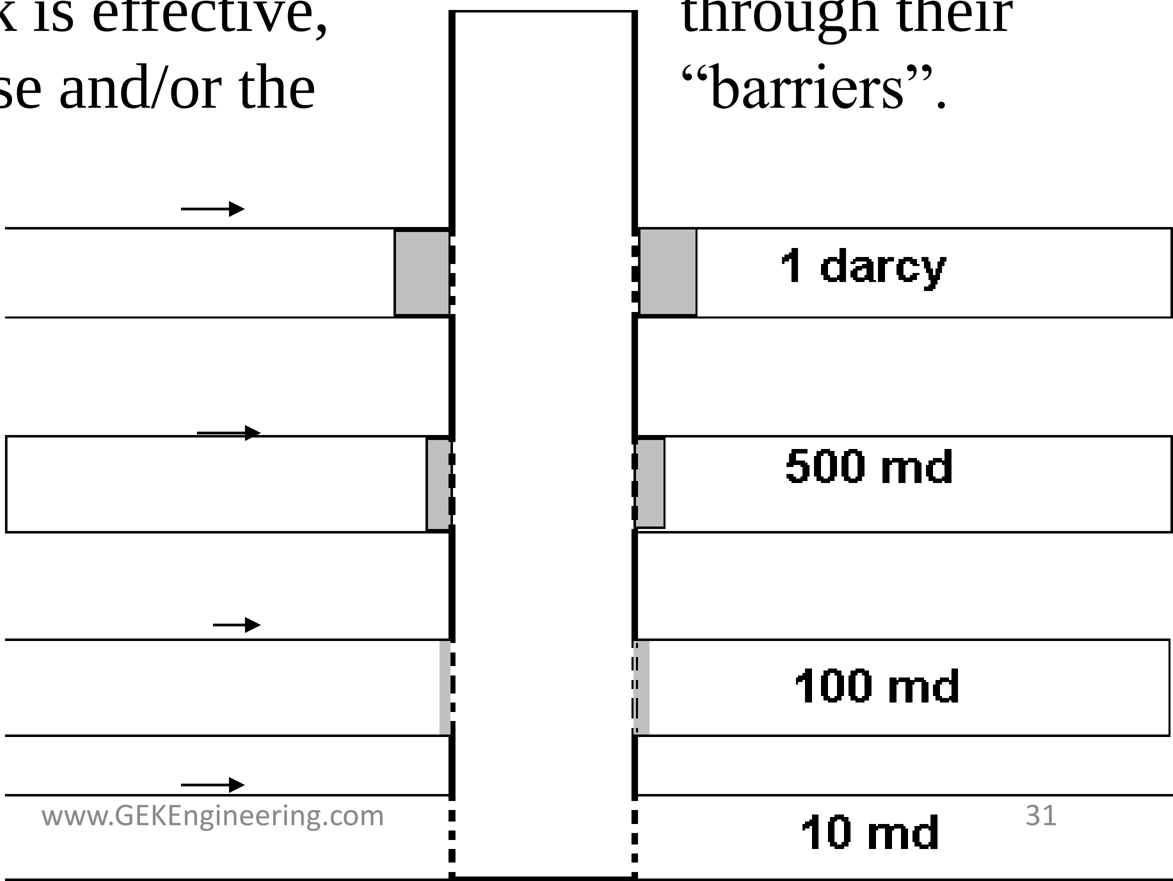


Diverting

By preferentially reducing the permeability of the high perm zones, there is a chance to force acid into the lower perm zones. When the block is effective, the injection pressure will rise and/or the injection rate will drop.

Most diverting agents still allow some flow through their "barriers".

Remember!   The blockage must be temporary unless the high perm zones have watered out.



Leakoff Learnings: Variable Natural Fracture Widths

May open as injection pressure raised

- Permeability can increase by two orders of magnitude

May close as reservoir pressure declines

- Can decline to matrix permeability as it closes.

Acid Penetration Distance

- in wide fractures: 25 to 100 ft
- in narrow fractures: 5 to 20 ft
- in matrix: : a few inches?

This assumes even reaction – and the most acid will enter (and react) in the wider fractures.

Acid penetration down a fracture is limited more by leakoff than by spending rate.

Leakoff Learnings: Wormholes (uneven reaction)

- starts in a high permeability channel or fracture
- widens pathway as acid reacts
- holes become “rounder”
- limited by side branches (leakoff)
- Length? – few inches to a few feet. Higher acid viscosity limits leakoff.

Gases Used in Acidizing

- Why? – flow back assist (unloading energy)
- Gasses:
  - Nitrogen
  - Carbon Dioxide, CO_2, both added CO_2 and CO_2 from the acid reaction.
  - And - just a trace of dissolved oxygen (7 parts per billion) (this is not a factor in most operations)

Gas Volumes and Types

High Pressure Gas Wells – none needed?

Low Press Gas Wells - 100 to 700 scf/bbl depending on BHP

Type:

- Gas Well - Nitrogen or Carbon Dioxide
- Oil Well (above bubble point) - Carbon Dioxide
- Oil Well (below bubble point) – Nitrogen or Carbon Dioxide

Gas Considerations

- Nitrogen has less than 10% of the solubility of carbon dioxide in oil.
- On Backflow
  - Gas provides lift (choke needed for optimization??
  - Gas may create foams or other emulsions

Putting Acid To Work

- Identify the damage and match an acid or solvent to remove it.
- Find a way to get the treatment to the damage
- Find a way to remove the spent acid and other fluids and solids.

Wellbore cleanout

- Common problems (BUT, look at “why” first)
  - mud/cement/perf/complet. fluid particles
  - scale (acid sometimes)
  - paraffin (forget the acid)
  - emulsions (acid???)
  - sludges (a real thick emulsion, acids worsen)
  - tars (no acid here either)

Perforation Damage

- debris from perforating
- sand in perf tunnel - mixing?
- mud particles
- particles in injected fluids
- pressure drop induced deposits
  - scales
  - asphaltenes
  - paraffins

Near Well Damage

- in-depth plugging by injected particles
- migrating fines
- water swellable clays
- water blocks, water sat. re-establishment
- polymer damage
- wetting by surfactants
- relative permeability problems
- matrix structure collapse

Polymer Removal

- From: muds, pills, frac, carriers
- Stable? - for years
- Removal methods:
  - time at temperature, 1 week w/ breakers, but breakers often separate from polymer during job.
  - acid, small volume, 10% HCl, soak, but reaching damage is difficult
  - bleach (3% to 5%) - 5 to 15 gal/ft, soak, bleach is corrosive; has problems getting live bleach to damage
  - enzymes and bacteria - soaks, temp critical – good potential

Scale Removal

- $CaCO_3$ - HCl wash
- $CaSO_4$ - dissolver/converter - then acid soak
- $BaSO_4$ - some dissolvers (slow on pure material) - better mechanical methods such as jetting, milling.
- FeS_2 - good luck! - mechanical best option

Sludges?

- asphaltenes and irons are triggers
  - 500 ppm iron (or more)
  - 0.5% asphaltenes (or more)
- can be rigid
- don't need much energy.....
- Very, very hard to break
- Treatment – soaks with xylene and/or dispersants. Heat, energy and repeat applications help.