

## Acidizing – Causes of Failures

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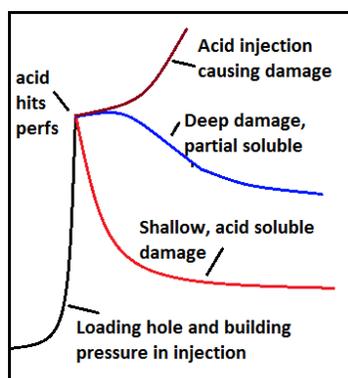
Acidizing is one of the oldest stimulation technologies in the oil and gas industry but when it is applied without sufficient knowledge of the target and well specific environment, it can cause more problems than it corrects. A survey of industry in the early 1990's by Carl Montgomery found a 70% failure to achieve expectations. The causes of acid failures are varied, but the reasons boil down to a handful of problems, acting singly or in concert.

### Acid Treatment Types

To simplify the operation, divide the acidizing methods into wellbore, matrix or fracture acidizing applications and the acids selected for use into hydrochloric or muriatic (HCl), hydrochloric/hydrofluoric (HCl/HF), and various organics, principally acetic (CH<sub>3</sub>COOH) and formic (HCOOH).

1. Wellbore acidizing is a wash of the wellbore to remove scale on the pipe surface, corrosion products such as rust, acid-soluble debris from drilling, completion, stimulation or production treating, or other acid-soluble particulates. There will be only minor leakoff from the wellbore to any formation. The most common acid used for wellbore washes is HCl and the typical concentration (by wt.) is 5% to 15%. The acid will contain an inhibitor (various compositions including quaternary ammonium salts) and often some type of a surfactant to strip oil from acid reactive surfaces. Solvents and oil dispersing surfactants are often necessary to break down, dilute, or disperse the two-phase to four-phase mixtures of oil, water, solids, and gas that are stabilized by viscosity of the mixture or of components, ionic charge or chemical emulsifier effect such as sulfates or other droplet or bubble film stiffeners. Main variables are:
  - a. correct treating fluid mixture for the target materials (which may vary widely in composition across the treated interval),
  - b. contact and enhancement of energy for mixing the treating fluid with the target (mixing, jetting, some forms of agitation, and/or heat),
  - c. sufficient volume of the treating fluid to accomplish the dispersion or solution,
  - d. time of contact that allows reaction to break physical, electric charge or physical bonding, and
  - e. follow-up displacement of the treated or dispersed mass from the wellbore before the problem composition can reform.
  - f. Placement of treating materials and keeping the materials on the damage are the largest problems in wellbore treating.
  - g. Diagnostics, such as a quick analysis of the recovered materials from the displacement after a wellbore treating wash can confirm the identity of the problem and can suggest solutions to prevent it from forming or optimize the treatment.

- h. The composition of what is initially preserved to organic damage often includes paraffin, asphaltic materials, corrosion products such as rust, formation fragments (fine silt), scale and water with only a very small amount of oil.
2. Matrix acidizing (or treating) is treating of the formation beyond the wellbore to remove permeability blocking damage to inward or outward flow. Most formation damage is very shallow, often within an inch or less of the formation face. Most common damage causes are particulates in injected fluids. Other causes are water blocks (relative permeability damage), fine particle migration (silts and clays), crush zones in perforations, bacterial colonies and any other blocking mechanism that is acid soluble or solvent and dispersant removable. Damage causes that cannot be removed by matrix treating include poor perforating practices (too few perfs, un-cleaned perfs, perfs off-depth), water influx (edge water or coning), packer slip or extremely low formation permeability. Before pumping an acid job under questionable conditions, re-perforating of the zone should be considered. Re-perforating is more controllable in terms of exact location affected and generally penetrates deeper than matrix acidizing.



Depth of damage can often be estimated by the injection pressure behavior as the acid reaches the formation face. If the pressure drops almost immediately as acid contracts the reaction face, then the damage is both acid soluble and very shallow. The following figure roughly illustrates the behavior. Note that deep damage, even when acid soluble, will react differently than shallow damage. Severe damage during acid jobs are rare but can happen if the acid cleans all the deposits in the tubing and tries to carry it into the pay zone. The pipe must be cleaned first.

Matrix acids and solvents are very much impacted by spending of acid strength or reaching saturation in solvents. Ability of acids and solvents to penetrate through the damage and reach the needed outward distance is a major problem. Delivery of the acid or solvent often requires pin-point injection through packers and wash tools that only allows injection into a selected number of perforations. Limited entry by controlled the number of perforations, the perf size and the rate of application may also work in some cases. The effectiveness of isolated delivery in a cased and cemented completion, of course, depends on how well the cement sheath isolates the areas between the perfs. If the acid is bullheaded without specific injection control, the acid will enter the highest permeability zones and the low permeability and damaged zones will not be treated.

Any reaction within the matrix, fissures or natural fractures of a formation is controlled by the area-to-volume ratio (AVR) and penetration of live acid by more than a few inches is very rare. AVR ratio in hydraulic fractures is on the order of 10:1, natural fracture AVR is ~100:1 to >1000:1 and matrix AVR is 20,000:1 to 30,000:1. Since acid is a first-order spending-rate

controlled reaction (acid spends as rapidly as it can reach the surface and its by-products can be removed), acid is often spent in the first few inches of formation contact. This cannot usually be modified by retardation means (those are reserved for some acid fracture methods).

Matrix acidizing may use HCl in carbonates (limestones, chalks, dolomites, etc.) and some limey sandstones (especially with carbonate cement). Typical acid concentration is 5% to 15% HCl. Additives include inhibitors, specific surfactants, or perhaps a mutual solvent. Matrix acidizing in sandstones may use HCl/HF acid mixture if the HF is needed for removal of silicate-based clay or migrating clay or silt particles. HF is a specialty acid and must be handled with care (skin penetrant that contact with concentrated amounts might be associated with leukemia – unproven (?) but care is advised and sampling is by specialists only) . Typical concentrations of HCl/HF will range from 12% HCl and 3% HF (for drilling mud removal) and 8% to 14% HCl and 1% HF for matrix problems involving clay or clay problems with volcanic source component derivation. Volumes of acid usually range between 50 to 10+ gal/ft. Application pressure is less than fracturing gradient.

Backflow diagnostics should include sampling about every 50 bbls and analyzing for oil, solids content, iron (sludge potential, formation deposit, iron scale and corrosion check), and chromium (corrosion control check). 13 chrome tubing is very susceptible to acid attack and must have the correct inhibitors and mixing apparatus. Ion ratios (Ca:Mg, Fe:Cr, etc.) are useful for determining variation from trends and changes in the field from area to area.

3. Acid fracturing involves fracturing with HCl, usually 15% to 28% concentration. Additives may include inhibitor, gelling agents, breakers and surfactant. Application pressure is in excess of the fracturing gradient. The objective is to create a crack into a carbonate formation (lower limit is 70% acid soluble), and use the acid to etch stable channels in the fracture face that will stay open when the hydraulic pressure is removed. Deep and highly stressed chalks and other soft formations are not usually good acidizing candidates since the chalk will creep under stress and the channels will close.

Typical service company acid fracturing models are almost useless for predicting etched acid length. Most acid frac models only consider the acid reactivity, but ignore the changing permeability as the acid reacts and increases near-frac matrix permeability. Typical acid etched frac half-lengths are 50 to 100 ft. The dominant fracture length growth control is leakoff, which increases permeability and sharply increases leakoff. The acid frac improvement works relatively well for oil reservoirs of 20+ md permeability, but proppant fracturing will increase production in gas reservoirs, lower permeability oil reservoirs and most other applications.

Acid fracturing injection rates are usually 10 to 20+ bpm and the fracture treatment is very much like a hydraulic fracture treatment without the proppant. Acid spends quickly so there is little need, except in the coolest formations ( $T < 100^{\circ}\text{F}$ ) for shut-in after the completion of the job.

Diagnostics are mainly around short and long term performance. If the oil or gas production rate falls sharply in a few days or weeks, the fracture length (and general contact area) may be too low for the formation permeability ( acidized frac lengths are too short to stabilize production). In most comparisons of production, proppant fracturing (which is usually more expensive) will outperform acid fracturing.

## Acid Failure Causes

Many problems (most preventable) may cause the failure of an acid job to increase or recover lost production rates. Acid penetration is limited so penetration of any improved zone into the reservoir will also be limited. Acid will dissolve many materials but has no effect, or even has a detrimental effect on several more. Many operators use acid as a diagnostic tool, just to see if what they consider a damage problem is acid soluble. Acidizing is relatively cheap, and using acid as a diagnostic tool is acceptable in most cases, if the results are analyzed for what they reveal.

1. Acid spot checks are needed on a random basis:
  - a. % acid (HCl test only) – a hydrometer is used for most checks but send a sample to the lab on a regular basis. Titration is the most accurate acid strength test. Hydrometer and litmus papers can be fooled by slightly acid salt water . Acid strength should be +/- 1.5% of target strength. Some additives depend on a certain concentration of acid to work properly. Field checks have shown everything from 1% HCl in saltwater to 28% HCl being brought to the lease when 15% HCl was ordered.
  - b. Iron concentration should be less than 100 ppm. Higher iron concentrations turn the acid yellow to light green. Corrosion inhibitor may have a brown cast. Too much iron will catalyze sludge or emulsion formation.
  - c. Sulfate should be less than 100 ppm. Too much sulfate will form CaSO<sub>4</sub> in spent acid.
  - d. Particulates should be low (plugging issue).
  - e. There should be no chlorinated hydrocarbons in the acid (<5 to 15 ppm). This is a lab test and should be done on rare basis – when problems are suspected or a cheap acid is offered.
2. Do not use phosphoric acids in most formations, particularly where calcium is present. Calcium phosphate (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) is a precipitate that forms quickly. Although some inhibitors can slow the precipitation of calcium phosphate, the inhibitor is quickly adsorbed when the mixture flows through a rock and the calcium phosphate precipitates anyway.
3. Organic acids such as acetic and formic are used at 10% maximum concentration or less. Using too high a concentration of these acids leads to formation of a precipitate (which is slowly soluble in fresh water).
4. Other acids such as sulfamic, chloroacetic and citric have uses but are not used in pumped acidizing jobs, except as occasional additives. Chloroacetic and sulfamic can be used to create a

slightly acid environment downhole to remove acid soluble materials. The form may be as acid sticks or acid balls (for horizontal and highly deviated wells where a stick would not drop.

5. Sulfuric acid forms sulfate scales with calcium, barium or strontium and is avoided. Nitric acid can form explosive compounds in oil and gas environments. By products from acids cannot be prevented with inhibitors because of adsorption and loss of the inhibitors.
6. The tubulars through which the acid will flow must be cleaned prior to the acid job with a pickling soak or flush or abrasive cleaning and the removed deposits moved out the path of the acid. Failure to clean the tubing will cause the acid to react with the deposits and carry any suspended materials to the face of the pay zone, causing significant damage. The type of "pickling" flush depends on the pipe and the deposits. Use of coiled tubing can by-pass the problem, but the CT needs to be pickled before the job.
7. Acid will dissolve calcium carbonate scale, some powdered cement, some forms of iron based scale and a few other minerals or solids in the formation or the completion steps. Acid has no effect on paraffin, asphaltenes, most clean sandstones, and most pure sulfate scales (calcium sulfate, barium sulfate, strontium sulfate, some iron sulfides, etc.). Sulfate scale mixtures may show acid reactions but most pure sulfate scale do not.
8. Iron sulfide may or may not be slowly soluble in HCl depending on its formula. Reaction rate, on even the soluble forms) is highly affected by area-to-volume ration and definitely slowed by increased scale thickness.
9. Matrix acidizing may improve permeability in the first few inches of an un-fractured carbonate reservoir, or by removing acid soluble damage in many types of reservoirs, but cannot penetrate deeply (more than a few inches).
10. Acids containing HF should not be used in carbonates or limey sandstones. The immediately formed precipitate  $\text{CaF}_2$  is basically insoluble. In low calcium content sandstones, an HCl preflush precedes the HCl/HF application. A preflush of ammonium chloride is needed to separate any acid with HF from salt waters.
11. Acidizing in formations with illite rims (fragile clay deposits that remain after the host grain has dissolved) can release particles that plug pores. Somewhat common on the Louisiana coast.
12. fibrous or spider web illite, particularly from the North Sea reservoirs, can react negatively with HCl or HCl/HF. Testing with core is advised.
13. If the formation water contains more than 500 ppm Fe, or the spent acid contains more than 500 ppm Fe, and the oil from the formation contains more than about 0.25% asphaltenes, the spent or nearly spent acid can (and often does) form a highly damaging, extremely high viscosity sludge. Iron must be controlled in these cases. Always test with a field sample of the water and a core fragment from the formation. Test oils from zones before acidizing.
14. Acidizing formations that were drilled with oil based mud (OBM) can create a highly damaging sludge. The worst OBM are those above 12 lb./gal mud density. The damage is so severe that it can take a 10mmscf/d flow to too small to measure. A dispersant or solvent flush and recovery must precede the acid to avoid the silt & cuttings-stabilized sludge. When testing for this potential problem, DO NOT USE LABORATORY SAMPLES OF OBM. Use only circulated field samples of OBM that have the cuttings. Use spent, partially spent and fully spent acid will all the additives.

15. Acidizing fractured carbonates that have authogenic clay in the fractures can turn loose sufficient particles to completely block permeability (some of the Santa Rosa limestone has this problem).
16. Acidizing CaSO<sub>4</sub> can lead to quick precipitation of a related mineral.
17. Acidizing after a scale converter treatment and before fluid flowback can lead to very rapid non-crystalline scale precipitation that can plug flowlines or tubing.
18. Most acid corrosion inhibitors are dispersible in mineral acid but not soluble in the acid. Agitation of the acid and inhibitor must continue during storage and pumping. Failure to effectively mix the acid will cause raw acid to be injected first (with severe corrosion potential) and pure corrosion inhibitor (last thing pumped) to then follow and coat the formation. Corrosion inhibitor is extremely damaging to the formation.
19. Some ions such as sulfur will require additives to control precipitation.
20. Avoid using many additives – get the information needed to only use what is needed. Typically 2 to 3 additives are all that is needed.
21. Acid must be injected in specific intervals to be effective. Pin-point injection or straddle packers (inflatable or cup type) are often the best diverting method if the cement sheath is isolating the zone. Particulate diverters are much more difficult to use and usually less effective. Large particulate diverters are usually poor diverters if the formation permeability is low (the permeability of a rock salt diverter perforation-sized tube, for example, is 600 md).
22. Cheap acid is sometimes offered, but the acid may contain chlorinated hydrocarbons that are refinery catalyst poisons. These materials may partition to the oil phase and the crude may cause damage, may be refused or may require significant cleaning.
23. HCl/HF jobs should not be shut-in for any time longer than that required to flow the well back. Hexafluorosilicate precipitates can form from HF reaction by-products if the HCl component is spent. Reduction of the HF strength and increasing the HCl is a control step.
24. Use of excessive volumes or strengths of HCl for the specific environment can lead to pipe damage. The inhibitor, even when properly dispersed, will adsorb in the formation and any returning live acid will damage the pipe during recovery.
25. Acid backflow should be tested on the first few jobs in an area.
  - a. Returning acid strength should be below pH 1.8 to 2.0 but less than 1% HCl to minimize corrosion and stop iron precipitation before the separators.
  - b. Analyze iron content to determine proper loading of iron reducer (don't use a chelating agent for jobs where the pH rises above 2.0 (iron hydroxide precipitation avoidance).
  - c. Check for solids. If dispersed or suspended solids are not being recovered, an acid flowback aid is needed (usually gas and/or a foamer applied in the overflush).
  - d. Analyze any precipitate seen in the backflow (iron hydroxide is ignored but increase iron control if needed).
  - e. Look for presence of emulsions. If the emulsion breaks quickly, ignore it. Otherwise test to see if a demulsifier or non-emulsifier is required.