

## Treatment in Oil and Gas Operators

### Background

Oil and gas operators have used acid treatment (acidizing) to improve well productivity for almost 120 years. Acidizing predates all other well stimulation techniques, including hydraulic fracturing which was not developed until the late 1940s. However, until the early 1930's, acidizing use was limited by the lack of effective acid corrosion inhibitors to protect the steel tubulars in the wells. With the development of effective corrosion inhibitors, the use and further development of acid treatment (acidizing) of oil and gas wells proliferated, leading to the establishment of the well stimulation services industry. Today, acidizing is one of the most widely used and effective means available to oil and gas operators for improving productivity (stimulation) of wells. Acidizing is commonly performed on new wells to maximize their initial productivity and on aging wells to restore productivity and maximize the recovery of the energy resources.

### Acidizing Basics

Acidizing involves pumping acid into a wellbore or geologic formation that is capable of producing oil and/or gas. The purpose of any acidizing is to improve a well's productivity or injectivity. There are three general categories of acid treatments: **acid washing; matrix acidizing; fracture acidizing.**

**In acid washing**, the objective is simply tubular and wellbore cleaning. Treatment of the formation is not intended. Acid washing is most commonly performed with **hydrochloric acid (HCl)** mixtures to clean out scale (such as calcium carbonate), rust, and other debris restricting flow in the well. Matrix and fracture acidizing are both formation treatments.

**In matrix acidizing**, the acid treatment is injected below the formation fracturing pressure. In fracture acidizing, acid is pumped above the formation fracturing pressure.

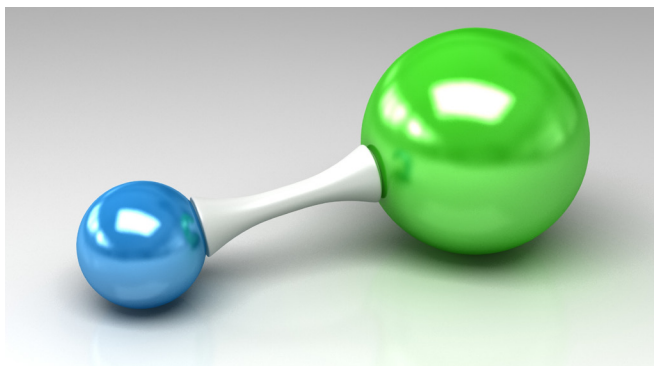
The purpose of matrix or **fracture acidizing** is to restore or improve an oil or gas well's productivity by dissolving material in the productive formation that is restricting flow, or to dissolve formation rock itself to enhance existing, or to create new flow paths to the wellbore. Two key factors dominate the treatment selection and design process when planning an acid job; formation type – carbonate, sandstone, or shale, and formation permeability – the ability of fluid to flow through the formation in its natural state.

Formation type determines the type(s) of acid necessary and formation permeability determines the pressure required for pumping the acid into the formation.



## Formation Type

Knowing the type of formation being acidized and details of its composition (mineralogy) is critical to achieving positive results. In carbonate formations, the acid job design is typically based on the use of **hydrochloric acid (HCl)**. The objective when acidizing carbonate formations



**Hydrochloric Acid (HCl) Molecule**

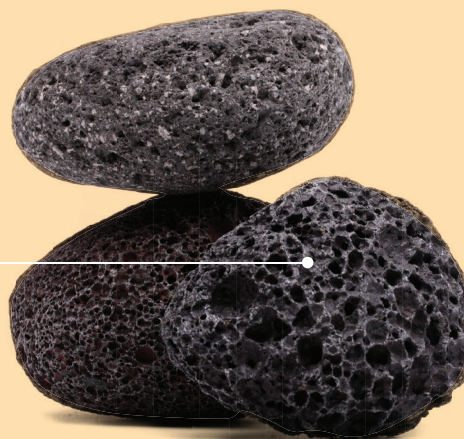
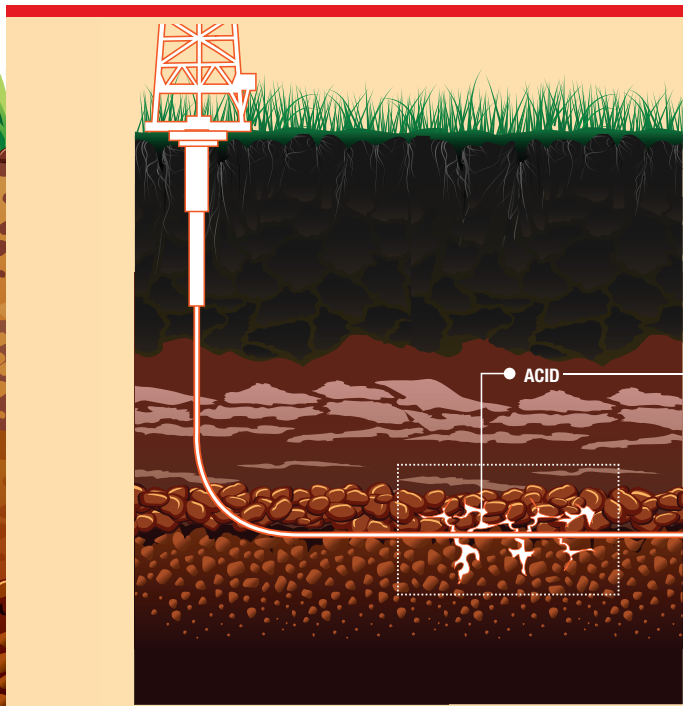
is to dissolve carbonate based materials to create new or clean existing pathways or channels that allow the formation fluids (oil, gas, and water) to flow more freely into the well. In sandstone formations, the acid job design is typically based on the use of hydrofluoric acid (HF), also known as mud acid, in combination with HCl. Sandstone minerals are not appreciably soluble in HCl alone but are much more so in mixtures containing HF. The objective when acidizing sandstone formations is to dissolve fine

sand (quartz), feldspar, and clay particles that are blocking or restricting flow through pore spaces, thereby allowing the formation fluids to move more freely into the well. If a sandstone formation contains appreciable carbonate minerals, then HCl may be added to the treatment.

Geologic formations are rarely completely homogeneous. They contain impurities and can be highly variable in their composition. As a result, designing an effective acid job can be complex. Most simple acid job designs use blends of HCl and HF to respond to the heterogeneous nature of geologic formations. The strengths of the acids and their volumetric ratios (HCl:HF) are based on the detailed mineralogy of the formation being treated. Other additives that are commonly used in an acid job include a corrosion inhibitor to protect the well tubulars and related equipment that is exposed to the acid, an emulsion blocker (surfactant) to prevent formation of oil-water emulsions, and an “iron-control agent” to retain any dissolved iron (e.g., rust) in solution. Other more specialized additives and different types of acids may also be used based on the case specific conditions or needs.

## Formation Permeability

Formation permeability determines the pumping pressure required to place the acid into the formation. In general, the lower the permeability, the higher the pumping pressure. In high permeability formations the acid can be pumped into the matrix of the formation at relatively low pumping pressures. If the pumping pressure is below the formation fracture pressure, the treatment is called “matrix acidizing.”



Dissolve carbonate materials; which creates new or clean existing pathways or channels that allow the formation fluids (oil, gas, and water) to flow more freely into the well.





In lower permeability formations the acid cannot be pumped into the formation matrix as readily, but is pumped through existing or induced fractures at higher pumping pressures. If the pumping pressure is above that which will part or fracture the formation, the treatment is called “**fracture acidizing**” (or “acid fracturing”).

There is not an absolute value of formation permeability that separates matrix and fracture acidizing, however the range of values where this may typically occur is between 0.1 millidarcies and 10 millidarcies, depending on the case specific situation. There are two subsets of fracture acidizing. The first type is performed as a preliminary step in a hydraulic fracturing operation, such as in shale or extremely low permeability sandstone or carbonate

formations. In this case, acid (HCl or HCl/HF blend) is pumped ahead of the fluid carrying the proppant that will hold the fractures open once the pump pressure is released. The purpose of the acid job in this case is to provide the cleanest possible formation face to enable easier fracture creation and maximize the performance of the proppant once it is placed. The second type is a fracture acid job, primarily applicable in carbonate formations, where the acid is pumped alone or following a fracturing fluid stage – with the intent of creating new or opening existing fractures, and dissolving formation material to create irregular fracture surfaces that create new flow paths or enhance existing flow paths into the wellbore when the fractures close.

## Operational Considerations

As mentioned above, acidizing oil and gas wells is a routine practice that has been used for a very long time. As a result, oil and gas operators and their service providers have considerable expertise and experience in safely and effectively conducting this work. Similarly, regulators that steward oil and gas operations have developed a well-founded regulatory framework to manage this work, protect the environment, and protect public health and safety.

The volume of acid used in an acid job is generally determined by the length of the formation (footage) being treated in the well. Acid volumes used per foot of formation can vary depending on the design objectives and the characteristics of the specific formation. Typical acid volume ranges are between 10 and 500 gallons per foot. While a volume of 500 gallons per foot may appear







to be large, in a matrix acid job, assuming 25% porosity, the acid would be displaced less than 20 feet from the wellbore. In fracture acid jobs, the acid will be displaced further, but is still limited by the fracture length. Fracture lengths are usually a few hundred feet at most.

**When acidizing**, the acid is chemically consumed and neutralized as the target material is dissolved. In carbonate formations the reaction is relatively simple and occurs in a single step. The hydrochloric acid (HCl) reacts with the carbonate to form a salt, carbon dioxide, and water. When acidizing sandstones with HF the reactions are more complex, occurring in three stages. In the primary stage, the mud acid reacts with the sand, feldspar and clays to form silicon fluorides and aluminum fluorides. In the secondary stage the silicon fluorides can react with clay and feldspar to release aluminum and silicon precipitates, however with proper design, formation of these damaging precipitates, which can restrict flow of oil or gas through the formation, can be avoided. In the final stage the remaining aluminum fluorides react until all the remaining acid is consumed.

Geologic formations are rarely homogeneous (pure carbonate, sandstone, or shale) but will be a blend of carbonate, sandstone, and clay minerals. As a result, most acid jobs are composed of both hydrochloric and hydrofluoric acid, with the ratios and strengths depending on the mineralogy and temperature of the formation being treated. Other types of acids can be used in more specialized situations (e.g., organic acids such as acetic and formic acid as alternatives to hydrochloric acid).

Additionally, specialized additives can be included in cases where specific chemical reactions are anticipated to be particularly severe and require control or mitigation.

A challenge in performing acid jobs is ensuring the acid goes where it can do the most good. To facilitate placement of the acid across the entire target interval in the well, operators often use coiled tubing units. A coiled tubing unit is a specialized piece of equipment that utilizes a reel mounted tubing string that can be run concentrically inside the well's production tubing to the point directly across the interval that is targeted for treatment. The acid is pumped through the coiled tubing and into the productive formation. This equipment allows precise placement and pumping of the acid. It also provides the added benefit of not exposing the production tubing to the acid.

When pumping any fluid into a well it will have a natural tendency to follow the path of least resistance and flow into those parts of the formation with the highest permeability. In an acid job, this is not the most desired result since the objective of an acid job is to improve the permeability of a well by dissolving material from lower permeability or plugged areas. To direct acid to the lower permeability parts of the formation, either chemical or physical flow diverters can be used. Use of diverters forces the acid into those lower permeability sections and thereby provides the potential for the most positive results.

In all cases, once the acid job has been pumped the well is brought on production. When this is done, the spent acid is produced along with the oil, gas, and water in the formation. Since the acid is chemically consumed when it contacts the formation, the recovered fluid is relatively benign.





## Environmental Management Considerations

As already mentioned, the oil and gas industry has been using acids for well treatment for well over 100 years. As a result, the industry has a great deal of experience with the safe and environmentally sound handling and management of these fluids both before and after their use. Operator, service companies, and regulatory agencies have sound procedures in place that protect both workers and the public.

Acids must be transported and used with proper precautions, safety procedures, and equipment. Transportation of the acid and related materials must be done in USDOT (or equivalent) approved equipment and containers, properly labeled, and follow approved routes to the work site. Personnel working directly with the acids must utilize the personal protective equipment (PPE) specified in the Safety Data Sheet (or equivalent) and be properly trained and experienced in the use of these materials.

All equipment used in pumping the acid should be well maintained and all equipment components that will be exposed to pressure during the acid job should be tested to pressures equal to the maximum anticipated pumping pressure plus an adequate safety margin prior to the start of pumping operations, in accordance with industry standards and pressure pumping service provider operating guidelines. The operator should consider the use of barricades to limit access to areas near acid and additive containers, mixing and pumping equipment, and pressure piping.

After the acid job is successfully pumped and the well is brought to production, the operator should consider using separate tanks or containers to isolate the initial produced fluids (spent acid and produced water). The fluids that are initially recovered will contain the spent acid (acid that is largely chemically reacted, neutralized, and converted to inert materials) and it will typically have a pH of 2-3 or greater, approaching neutral pH. These fluids can be further neutralized to a pH > 4.5 prior to introduction into the produced water treatment equipment, if necessary. Once neutralized, the spent acid and produced water can be handled with other produced water at the production site. Most produced water, including spent acid, is treated as needed and then injected via deep injection wells that are permitted by the jurisdictional regulatory authority.

## Conclusions

- Oil and gas operators have safely and successfully used acid to improve productivity of oil and gas wells for nearly 120 years. Today, acidizing is one of the most widely used processes for stimulating oil and gas wells.
- Two types of acids are most commonly used; hydrochloric acid in all formation types and hydrofluoric acid in sandstones and certain shales. Other types of acids, such as organic acids, may also be used in specialized situations.
- Since geologic formations are never homogeneous, blends (particularly for sandstone formations) of HCl and HF are usually pumped with the blend ratios based on the formation mineralogy.
- All aspects of the regulatory framework surrounding the use of acid in oil and gas wells are well developed and mature as are the operational and safety practices employed by operators and service providers.
- When the acid reacts with formation materials it is largely consumed and neutralized.
- Spent acid that is recovered when a treated well is brought on production is treated and safely disposed of in essentially the same way as produced water.

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