

Matrix Acid Stimulation

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Abstract

Matrix acid stimulation is a relatively simple technique that is one of the most cost-effective methods to enhance well productivity and improve hydrocarbon recovery.

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Acids attack steel to produce solutions of iron salts while generating hydrogen gas.

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Introduction

Matrix acid stimulation is a relatively simple technique that is one of the most cost-effective methods to enhance well productivity and improve hydrocarbon recovery. The science of acidizing originated more than 100 years ago when Herman Frasch of Standard Oil patented the use of hydrochloric acid (HCl) to stimulate carbonate formations. One of his colleagues patented the use of sulphuric acid for the same purpose. After a flurry of activity, neither technique was applied on a widespread basis during the next 30 years.

The effect of the treatment on production was positive, if not spectacular, and provided the impetus to perform more treatments. Some of the later treatments produced excellent results, and news of the technique quickly spread. In the same decade, attempts were made to improve production from sandstone reservoirs by injecting mixtures of HCl and hydrofluoric (HF) acid. These early treatments were not particularly successful, and the HCl/HF mixtures were relegated to only occasional use in wells with drilling mud damage.

It was not until the 1960s that treatments containing HF again saw widespread use in well remediation when studies on chemical interactions of HF with typical sandstone formation materials and guidelines for treatment optimization were published. Despite the elimination of much of the mystery surrounding the use of HF, acidizing sandstone formation remained a hit-or-miss enterprise. It was very successful in some areas and totally disastrous in others.

Chemistry

In the early days of acidizing, wellsite quality control was almost nonexistent, and little attention was paid to such variables as acid strength. Improved understanding initially came from empirical observations in the field followed by extensive research and development work carried out by thousands of scientists and engineers. Core flow studies, geological and mineralogical investigations, reaction kinetics, physicochemical modeling of the propagating reaction front, solubility testing, and reaction products analysis are some of the many aspects of matrix acidizing that have been investigated. Sophisticated modern-day analytical techniques, coupled with computer modeling, have allowed detailed examination of the acidizing process to provide a better understanding of potential pitfalls and how to avoid them.

Acid System Design

Carbonate acidizing is usually performed with HCl except in situations where temperatures are very high and corrosion is an issue. In such situations, organic acids like acetic or formic acids are used because they are much less aggressive. Occasionally, it may be beneficial to retard acid formulas, slowing their reaction rate to allow deeper penetration of live acid or preferential creation of large wormholes through any near-wellbore damage.

Selection of an appropriate acid design for sandstone formations is a more esoteric matter. Part of this problem stems from the complex and heterogeneous nature of most sandstone matrices. Interactions between the many different mineral species and the injected acid depend not only on the chemical composition of both but also on temperature, pressure, surface morphology, pore size distribution, and pore-fluid composition.

Over the years, many different acidizing systems have been developed for specific applications. In general, the three principal drivers for these developments have been (1) the desire to retard the acid/mineral reactions, thereby achieving greater penetration; (2) the desire to make the acid less aggressive to tubulars, wellheads, and screens; and (3) the desire to avoid undesirable reactions that could result in formation damage. Some approaches used to retard the acid have included buffered HF systems or organic systems, fluoroboric acid, and mixtures of esters and fluorides to generate HF in situ by thermal hydrolysis. Other, more exotic efforts have included the use of hexafluorophosphoric acid or hexafluorotitanic acid. For carbonate acidizing, mixtures of esters with enzymes have been used to generate organic acids in situ. In general, systems that generate acid in situ or that use organic acid blends also address the problem of corrosion, but such systems may still cause corrosion problems on flowback if they contain no inhibitors.

Mitigating undesirable reactions or their byproducts has spawned many proprietary formulas as well as changing some of the application guidelines used in matrix acidizing. The old generic acids consist of mixtures of HCl and HF acid, known in the industry as mud acid. Traditionally, the HCl/HF ratio was 4:1. However, it has been suggested that it may be necessary to increase this ratio to as much as 9:1. The rationale for these relatively high HCl/HF ratios is that dissolution of clays by HF mixtures produces many secondary reaction products that can reprecipitate in the formation and cause damage. These damaging reaction products are slightly more soluble if the pH is kept low throughout the treatment and during flowback. New acid systems have been developed that do not reduce the useful life of well tubulars, and excess HCl is no longer required to reduce secondary precipitates.

Corrosion Inhibitors

Acids attack steel to produce solutions of iron salts while generating hydrogen gas. Depending on the steel metallurgy, type of acid (mineral or organic), acid strength, and temperature, the reaction may be more or less vigorous. This attack can lead to removal of a substantial amount of metal mass, potentially shortening the lifespan of well tubulars. It was the discovery of an effective corrosion inhibitor that sparked the widespread application of acidizing in the 1930s. That first inhibitor was based on arsenic, and, while efficient, its use was discontinued because of concerns over toxicity and the environment. A variety of organic inhibitors superseded the early arsenic compounds. The majority of these are based on acetylenic alcohols, like octynol and propargyl alcohol, highly reactive molecules containing

a carbon-carbon triple bond. The ability of these materials to protect steel is dependent on the proper dispersion of the hydrophobic alcohol in the acid because the protection mechanism involves creation of an inhibitory film on the metal surface. Environmental legislation has forced a re-evaluation of many corrosion inhibitors. There is some indication that the most effective way to acidize high-temperature wells is to use organic acids like formic and acetic instead of mineral acids because they are much easier to inhibit and are relatively cost competitive and biodegradable.

Iron Control Agents

Iron is plentiful in any oilfield operation and is perhaps the most underestimated problem in acidizing. In general, clean steel dissolves to produce ferrous ions, but these can be converted to the problematic ferric ion by dissolved oxygen. Several iron reaction products can precipitate from acid as it spends and the pH rises. The most likely to precipitate is ferric hydroxide, which forms a gelatinous plugging precipitate when the acid pH rises. The most common chemical methods used to address the issue of iron precipitation include chelation/sequestration and reduction. Sometimes, combinations of different reducing agents are used to provide iron control while minimizing any risk of unwanted byproducts.

Clay Stabilizers

Sandstone formations are heterogeneous with quartz as the primary skeletal mineral and various carbonates, clays, or feldspars acting to cement the sand grains together. In addition, clay minerals may be suspended in the pore filling fluid or may line the pore spaces. These clays can react by ion exchange or partial dissolution when contacted by injected fluids. Often, this results in the disaggregation, disintegration, or swelling of the clay and can plug the pore spaces and pore throats. Many acidizing formulas contain clay stabilizers to mitigate the problem. The simplest clay stabilizers are salts such as ammonium and potassium chloride; however, potassium chloride cannot be used when HF is used because of the risk of secondary precipitates like potassium fluorosilicate. It is much more common to incorporate any one of the several synthetic materials that prevent clay swelling in the treating fluids. These materials are usually cationic, like quaternary amines or polymers with similar active groups.

Other materials have been used to prevent the migration of mobile clays or silica fines through the matrix because these can cause problems if they accumulate in the near wellbore. One approach has been to modify the acidizing system by replacing simple HF with fluoroboric acid, which is slowly hydrolyzed into HF, reducing the reaction rate of HF and helping to fuse clay platelets together.

Surfactants

Surfactants encompass a very diverse group of chemicals including foaming agents, water-wetting agents, oil-wetting agents, emulsifiers, demulsifiers, and antisludge agents. All these agents have effects on surface and/or interfacial tension. Water-wetting surfactants lower the surface tension of aqueous fluids to improve the ability of the treating fluid to penetrate small pores and to react with the matrix constituents. Surfactants also improve the recovery of these

same fluids after the treatment. It is a widely accepted practice to include water-wetting surfactants in almost all matrix acid treatments. Demulsifiers and nonemulsifiers are designed to prevent or facilitate the breakup of the emulsions that tend to form between crude oil and live or spent acid fluids. Such emulsions can be very viscous, even quasisolid, and may plug the pores of the treated matrix.

Diverting Agents

A certain volume of acid is allowed to flow into and remediate the higher permeability intervals, and then, the flow is diverted to lower permeability zones. The most common materials used to divert the acid are particulates that are insoluble in acid, but soluble in hydrocarbons for easy cleanup. Such agents include benzoic acid, naphthalene, oil-soluble resin, gilsonite, and wax beads. Other systems have included polymers that crosslink as pH or calcium ion level rises. Foaming agents are widely used in acidizing treatments to provide diversion.

Another diverting technique is to use some selective isolation tool such as a straddle packer or sets of opposing cups to bracket the interval exposed to the acidizing fluid. Recently, jetting techniques have been used to improve placement selectivity of stimulation fluids in gravel-packed completions.

Conclusion

1. Matrix acidizing, with the appropriate systems in correctly identified candidate wells, is the most cost-effective way to enhance oil production in sandstone and carbonate reservoirs.
2. Increased understanding of the chemistry and physics of the acidizing process as well as improvements in wellsite implementation have resulted in better acidizing success.
3. Use of computer software that includes all known rules and guidelines for sandstone acidizing can greatly improve the success ratio by eliminating inappropriate designs and standardizing treatments.
4. New acid systems with improved performance were developed specifically to address many of the problems inherent in sandstone acidizing.

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