

Acidizing Oil and Gas Reservoirs: Current Practice and Applications of the Arcasolve Acidizing Process

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1. Introduction

Acid treatments have been applied to wells in oil and gas bearing rock formations for many years. Acidizing is probably the most widely used work-over and stimulation practice in the oil industry [1].

By dissolving acid soluble components within underground rock formations, or removing material at the wellbore face, the rate of flow of oil or gas out of production wells or the rate of flow of oil-displacing fluids into injection wells may be increased.

2. Conventional Acid Systems

A number of different acids are used in conventional acidizing treatments, the most common are:

- Hydrochloric, HCl
- Hydrofluoric, HF
- Acetic, CH₃COOH
- Formic, HCOOH
- Sulfamic, H₂NSO₃H
- Chloroacetic, ClCH₂COOH

These acids differ in their characteristics. Choice of the acid and any additives for a given situation depends on the underground reservoir characteristics and the specific intention of the treatment, for example near well bore damage removal, dissolution of scale in fractures, etc.

The majority of acidizing treatments carried out utilize hydrochloric acid (HCl). *However, the very fast reaction rate of hydrochloric acid, and other acids listed above, can limit their effectiveness in a number of applications.*

All conventional acids including HCl, and organic acids react very rapidly on contact with acid sensitive material in the wellbore or formation. Wormholing

is a common phenomenon. The rapid reaction means the acid does not penetrate very far into the formation before it is spent. Conventional acid systems are therefore of limited effectiveness in treatments where deep acid penetration is needed. Problems in placing acid are compounded in long horizontal or directional wells. In these wells it is difficult to achieve truly uniform placement of acid along the well-bore, which may be several thousand metres long, let alone achieve uniform stimulation of the surrounding formation.

There was an early recognition that it was desirable to delay the rate of reaction of the acid and a variety of techniques have been developed to achieve this. Patents relating to several of these techniques have been issued. Further information on these retarded acid systems is given below.

3. Retarded Acid Systems

Methods which have been developed to slow the acidizing process include:

- Emulsifying the aqueous acid solutions in oil (or solvents such as kerosene or diesel fuel) to produce an emulsion which is slower reacting [3,4,5].
- Dissolving the acids in a non-aqueous solvent [6,7,8,9].
- The use of non aqueous solutions of organic chemicals which release acids only on contact with water [10,11].
- The use of solutions of methyl acetate which hydrolyses slowly at very high temperatures to produce acetic acid [12].

In addition to these methods, of which emulsifying the acid is probably the most important, some retardation of the reaction rate can be achieved by gelling the acid or oil wetting the formation solids.

3.a. Gelled Acids

Gelled acids are used to retard acid reaction rate in treatments such as acid fracturing. Retardation results from the increased fluid viscosity reducing the rate of acid transfer to the fracture wall. Use of the gelling agents (normally water soluble polymers) is limited to lower temperature formations as most gelling agents degrade rapidly in acid solution at temperatures above 130°F (55°C) [2].

Gelling agents are seldom used in matrix acidizing because the increased acid viscosity reduces injectivity and may prolong the treatment with no net benefit i.e. the slower injection rate counters the benefit of a reduced reaction rate.

3.b. Chemically Retarded Acids

These acids are often prepared by adding an oil-wetting surfactant to the acid in an effort to create a physical barrier to acid transfer to the rock surface. In order to achieve this the additive must adsorb on the rock surface and form a coherent film.

Use of these acids often requires continuous injection of oil during the treatment. At high flow rates and high formation temperatures, adsorption is diminished and most of these materials become ineffective [2].

3.c. Emulsified Acids

Emulsified acids may contain the acid as either the internal or the external phase. The former, which is more common, normally contains 10 to 30 percent hydrocarbon as the external phase and 15% hydrochloric acid as the internal phase. When acid is the external phase, the ratio of oil to acid is often about 2:1. Both the higher viscosity created by emulsification and the presence of the oil can retard the rate of acid transfer to the rock surface. This reduction in mass transfer rate, and its corresponding reduction in acid reaction rate, can increase the depth of acid penetration into the rock formation before the acid reacts with the rock or damaging material [2].

Use of oil external emulsified acids may be limited by the increased frictional resistance to flow of these fluids down well tubulars [2]. The presence of surfactants in the acidizing fluid, to produce the emulsion, can affect the wetting characteristics of the rock formation i.e. change a water wet rock surface into an oil wet surface. This can necessitate remedial post acidizing treatments to restore the rock surface to a water wet state if successful oil production is to be attained.

4. Types of Acidizing Processes

Acidizing is used to increase production in many situations. The most important include damage removal, completion and stimulation of horizontal wells, matrix acidizing, fracture acidizing and gel breaking.

4.a. Damage Removal

Damaged wells are those which suffer a restriction in flow rate. This may be due to a number of causes, for example, drilling damage or build up of carbonate scale. Damage may occur at the wellbore face or as a zone of reduced permeability extending several inches or even feet into the formation which severely restricts productivity. *If the damage can be removed, very significant increases in production rate can be achieved.*

For example, if a damaged zone extends 6 inches into a formation and the damaged permeability is only 5% of the undamaged permeability, the affected well will only produce 30% of the production of an undamaged well. Removal of the damage will therefore result in a 3.3-fold increase in production rate [2].

Conventional acidizing processes may remove damage up to several inches into the formation but are generally not effective for treatment of deeper damage. Success in treatment of deep formation damage requires the use of highly retarded acids. *Arcasolve™ functions as a highly retarded acid suitable for removal of deep damage.*

The importance of damage removal is highlighted by the fact that the Society of Petroleum Engineers (SPE) now hold regular international conferences dedicated to this subject [12].

4.b. Completion and Stimulation of Horizontal Wells

Horizontal drilling is a technique which has been enthusiastically adopted by the oil industry since about 1988. Because the wellbore has a greater contact area with the oil bearing zone, much higher rates of production are possible compared to conventional vertical wells. Productivity at least 2-3 times that of vertical wells can generally be achieved. Despite higher costs, return on investment is better than for vertical wells in many circumstances.

The importance of horizontal wells is likely to increase further. The current trend is towards very long wells which can be up to several km in length. When bringing these wells into production, the effective clean up of drilling fluid damage is needed. This is particularly important in low permeability formations.

Newly drilled horizontal wells normally require acidizing to remove drilling mud damage before being brought into production. *The efficient placement of conventional acids is critical, especially in long horizontal sections [14].* Due to their fast reaction rate they need to be placed using coiled tubing, which is expensive, or using foam, gel or other diversion methods. Significant care has to be taken over treatment design when using diversion methods and there may be a problem with gel residues.

The difficulty of applying HCl in extremely long horizontal producing intervals to uniformly remove drilling damage has been identified by several operators as a very serious problem with the result being disappointing well productivity [15].

There is a need for improved acidizing methods which are effective for the removal of drilling fluid damage from long horizontal intervals. Arcasolve™ is effective for this application.

4.c. Matrix Acidizing

Matrix acidizing involves the use of acid injected at below fracture pressure.

It is normally used for the removal of skin damage associated with work-over, well killing or injection fluids, and by precipitation of scale deposits in tubulars, the wellbore or within the formation.

As stated in (4.a.) above, removal of near well bore damage can result in significant stimulation, by say three-fold. Treatment normally involves injecting 15% HCl followed by a sufficient afterflush of water or hydrocarbon to clear all acid from well tubulars. A corrosion inhibitor is added to the acid to protect tubulars during exposure to acid. Other additives, such as anti-sludge agents, iron chelating agents, de-emulsifiers and mutual solvents are added as required for a specific formation.

Matrix acidizing may also be used to increase formation permeability in undamaged wells. Where damage is thought to exist within the formation, the aim of the treatment is to achieve more or less radial acid penetration deep into the formation to increase the formation permeability around the wellbore. Deep penetration can only be achieved with retarded acid systems.

In undamaged formations even significant permeability increases over a 3 to 6 meter radius around the wellbore will result in less dramatic stimulation than achieved when removing damage. There is a practical limit of about a 50% increase in injectivity or productivity of undamaged oil or water wells which can be achieved using matrix stimulation.

Higher levels of stimulation would probably require the use of uneconomic volumes of stimulation fluid (acid or acid generating solution). Increases of less than 50% will probably be the norm. This is because the volume required to fill an expanding circumference is a squared function. If the depth of penetration is doubled the required volume increases 4-fold. Attempts to stimulate extended volumes of a reservoir will show a diminishing return per unit invested. It is important when designing jobs that a balance be struck between the volume pumped (cost of job) and the resulting increase in production.

Use of an acidizing system with a reaction so highly retarded that essentially no reaction takes place during the time that the acid is being pumped into the reservoir has been considered in mathematical terms. *This hypothetical system has been proposed as the ultimate for a matrix treatment [2]. Arcasolve™ (see section 5) approaches such a system.*

4.d. Fracture Acidizing

Fracture acidizing, also known as acid fracing is the most widely used acidizing technique for stimulating limestone or dolomite formations [2]. In an acid fracturing treatment a pad fluid is injected into the formation at a rate higher than the reservoir matrix will accept. This rapid injection produces a

build-up in wellbore pressure leading to cracking (fracturing) of the rock. Continued fluid injection increases the fracture's length and width. Acid (normally 15% HCl) is then injected into the fracture to react with the formation and create a flow channel (by etching of the fracture surface) that extends deep into the formation. This allows more reservoir fluid to drain into the wellbore along the new fractures once the well is put back on production.

The key to success is penetration of reactive acid along the fracture. This is more difficult to achieve in acid fracturing than in propped fractures (the other main form of frac treatment). Acid penetration is particularly important in low permeability carbonates which are frequently subject to scaling where small fractures meet larger fractures. *Acid fracturing methods which can achieve deep acid penetration offer tremendous potential to solve scaling problems [13].*

The effective length of an acidized fracture is limited by the distance that acid travels along the fracture before it is spent. This is controlled by the acid fluid loss, the reaction rate and the fracture flow rate [13]. This problem is particularly severe when the acid reaction rate is high owing to high formation temperature.

The acid fluid-loss mechanism is more complex than that of non-reactive fluids. In addition to diffusive leak off into the formation, flowing acid leaks off dynamically by dissolving the rock and producing wormholes. *Wormholes are very detrimental in fracture acidizing [13].* They greatly increase the effective surface area from which leak off occurs and are believed to affect acid fluid loss adversely. Acid leaks off predominantly from wormhole tips rather than the fracture face. As wormholing and excessive leak-off occur, the leak-off rate exceeds the pump rate, and a positive net fracturing pressure cannot be maintained to keep the fracture open. At this point in the treatment, which may be as soon as 6 minutes after starting to pump acid, the fracture extension slows or stops.

Acid fluid loss control has long been a problem in fracture acidizing. The most common techniques involve use of viscous pads or acid solutions. The principle behind these is to lay an impermeable filter cake on the fracture face and minimize wormholing. In practice these filter cakes are relatively ineffective in controlling acid fluid loss because of the quick penetration by wormholes and the constant erosion of fracture faces during treatment.

Fluids used in the fracture acidizing process (pad fluid, acid or additives) can be detrimental to well performance following the job. This can be due to clean up problems or a reduction in the formation permeability adjacent to the fracture.

Problems are particularly pronounced in the case of gas wells. A particular problem is the removal of high viscosity fluids. The time required to achieve cleanup increases significantly as fluid viscosity increases. For example, in a gas well in a 0.1 mD permeability formation, a fluid such as oil or water that has a viscosity of 0.25 cP at reservoir temperature is easily removed from the

formation. Maximum rate is attained after about 3 days. At 25 cP viscosity, maximum rate is attained after about 20 days. 250 cP fluid is difficult to remove from the formation and only 24% of the fracture fluid will have been produced after 400 days of production. Similar increases in cleanup time are seen as fracture length increases [2].

Ideally the best acid system for fracturing is one that only etches the fracture face by dissolution and leaks off into the formation mainly by diffusion [13]. It is also very desirable to be able to obtain deep penetration along fractures without resorting to the use of high viscosity components. Arcasolve™ has these characteristics.

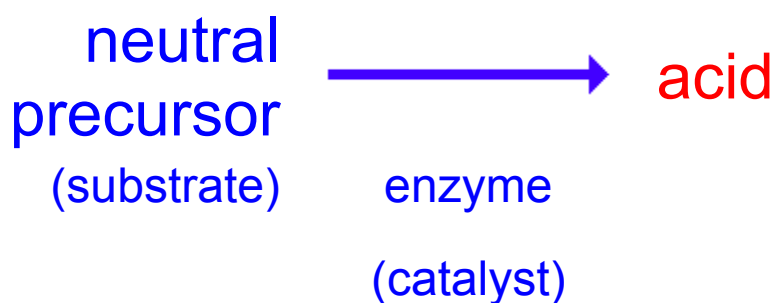
4.e. Gel Breaking

Acids are used to break acid sensitive gels used in propped fracture applications. The use of acid breakers in open hole horizontal well completions has recently been demonstrated [3].

5. Arcasolve™

Arcasolve™ is a patented acidizing method which uses acid precursors (which are not themselves acidic) in combination with a catalyst. The catalyst acts on the precursors to produce organic acid (normally acetic acid) *in-situ* following placement of the Arcasolve fluid within the wellbore or rock formation.

Basis of the Arcasolve™ process:



The amount of acid released, and the rate of release, can be controlled by using different Arcasolve™ formulations.

Arcasolve™ has a number of significant benefits:

- Deep penetration into the formation can be achieved
- Zonal coverage is excellent
- Uniform placement of acid along long wellbore intervals can be readily achieved with no fluid loss due to wormholing
- Fluid is very low hazard - biodegradable reactants and acidizing products ensure minimal safety and ecotoxicity issues in use and disposal
- Corrosion inhibitors are not required
- Fluid is low viscosity allowing rapid clean up post treatment
- Extent of acidizing (quantity of acid, rate of production) can be accurately controlled in contrast with other acidizing methods

Well test data and the results of independent laboratory evaluations is available for a number of different Arcasolve™ applications.

6. Use of Arcasolve™ in Acidizing Processes

Arcasolve™ can be used for a large number of acidizing applications including damage removal, completion and stimulation of horizontal wells, matrix acidizing, fracture acidizing, gel breaking and stimulation of natural fracture networks.

Use of Arcasolve™ is a simple procedure which is similar in all applications. An Arcasolve™ formulation is selected appropriate for the application (to produce the required amount of acid at a particular rate). The formulation is mixed at the wellhead and injected at the desired rate to fill the wellbore or the formation. After placement of the fluid the well is shut in and acid is generated *in-situ*. The well is then put on production.

6.a. Use of Arcasolve™ for Damage Removal

Arcasolve can evenly remove near wellbore damage along long intervals. It can also treat damage deep in the formation including sandstone reservoirs with deep carbonate scale, with potential for significant production improvements.

The effectiveness of Arcasolve™ at removing damage to carbonate formations caused by the use of water based drilling muds has been demonstrated in an independent study carried out by Stimlab (UK) with support from the UK DTI. Stimlab is a recognized source of expertise on

acidizing technologies. More recent Stimlab work has demonstrated that Arcasolve™ is also effective for the removal of oil based drilling mud damage from carbonate cores. Arcasolve™ may also be useful for the removal of dolomite (carbonate) weighted drilling muds from sandstone formations.

Removal of drilling damage restores the formation to its undamaged productivity allowing oil to be produced at its maximum rate. *The potential for the use of Arcasolve™ in remediation of mud damage resulting from drilling, particularly in horizontal wells (see below) has been clearly demonstrated (see Examples of Results of Arcasolve treatments). Significant gains in production have been achieved.*

6.b. Completion and Stimulation of Horizontal Wells

Horizontal wells are increasingly being used in oil and gas production and their importance is likely to increase further. *When bringing these wells into production, the effective clean up of drilling fluid damage along the whole of the production interval is needed. This is particularly important in low permeability formations.* This can be readily achieved with Arcasolve™. Because the Arcasolve fluid is not reactive when being placed, the wellbore can be filled before most of the acid is generated. Leak off into the formation is regulated by the filter cake or other damage and there is no fluid loss due to wormholing. Subsequent generation of acid ensures that all of the production interval is treated, with the same amount of acid being supplied to all parts of the wellbore. This results in effective cleanup.

The whole of the interval can be treated without a need for coiled tubing or diverters which are required for conventional hydrochloric acid treatments.

In addition to mud damage removal, if sufficient Arcasolve™ fluid is used to fill the wellbore and penetrate some distance into the formation an increase in the permeability of the formation can be achieved. The matrix stimulation of the formation can stimulate production above that which would be obtained even with complete damage removal.

Effective damage removal and matrix stimulation reduce payback periods and lead to increases in the net present value (NPV) of the well.

6.c. Use of Arcasolve™ in Matrix Acidizing

Matrix acidizing was the initial application for Arcasolve™. The permeability of carbonate rock formations is increased over a 10 to 20 foot radius around the wellbore, by placing the fluid and allowing the produced acid to dissolve a portion of the rock. **Increase in the permeability allows a greater rate of production of oil or gas** (or greater rate of injection of fluids in the case of injector wells used for pressure maintenance).

Very deep penetration of acid can be achieved if needed and the use of gels and surfactants, which might cause cleanup or wettability reversal problems is not needed.

As well as treating carbonate formations Arcasolve™ can be used to remove deep carbonate scale from sandstones.

Arcasolve™ comes very close to being the ideal system for matrix acidizing described in [2]. Depending on the pump rate, typically 90% or more of the acid is delivered after the fluid has been placed.

Matrix treatments designed to give a 20% increase in production rate (formation assumed to be undamaged) have given up to 80% increases in production (San Andres Dolomite, Texas) indicating effective damage removal even in wells considered undamaged.

6.d. Use of Arcasolve™ in Fracture Acidizing

Although not originally designed as a fluid for acid fracturing, the opportunity for Arcasolve™ in this application could be very significant. Arcasolve™ appears to possess many properties required from an acid fracturing fluid as shown in Table 1. Below.

Table 1. Comparison of Properties of Arcasolve™ with Desired Properties of Fracture Acidizing Fluid

Property sought in fracture acidizing fluid*	Properties of Arcasolve
Low viscosity	Low viscosity
Etches fracture face by dissolution	Etches fracture face by dissolution
Leaks off into formation mainly by diffusion	Leaks off into formation mainly by diffusion
Causes minimal formation damage	Arcasolve used to remove formation damage
No wormholing	No wormholing

* adapted from reference [13]

The comparison indicates that Arcasolve™ may represent an ideal fracture acidizing fluid, able to penetrate long distances, etch fracture faces, increase the permeability of the matrix where the fluid enters the formation by diffusion, and remove any existing formation damage. In addition the low viscosity of the fluid means that maximum production rate should be attained quickly following the treatment.

Because acid is produced over a period of several hours or longer, acid fracturing treatments using Arcasolve™ may need to be performed in a different way to existing acid fracturing treatments. Fractures would need to be held open for at least several hours and possibly up to a day. The pad fluid used in conventional treatments would probably not be needed - Arcasolve™ would be injected directly.

6.e. Use of Arcasolve™ in Gel Breaking

Gel breaking is another application for Arcasolve™ for which additional patents are granted or pending. *Arcasolve™ can be incorporated into acid sensitive gel systems such as borate cross linked guar so as to produce a complete break within a specific, desired time frame.*

Please contact Cleansorb if you wish to discuss this application further.

6.f. Stimulation of Natural Fracture Networks using Arcasolve™

Arcasolve™ may be used to effectively stimulate natural fracture networks. *Deep penetration along fractures can be achieved before acid is produced.* Laboratory evaluation to date has been positive. Field trials are currently being conducted in the Austin Chalk.

7. Comparison of Arcasolve™ with Other Acid Systems

7.a. Comparison to HCl

The rapid reaction between HCl and carbonate limits the penetration of HCl into carbonate formations. It is unlikely that HCl will remove deep formation damage and HCl is not suitable for deep matrix acidizing. *Arcasolve™ can penetrate deeply and is suitable for both applications.*

HCl is particularly corrosive to steel, aluminium or chromium plated equipment which are components of many pumps. Expensive corrosion inhibitors need to be used in these circumstances. This cost becomes very significant when treating formations at higher temperatures due to the requirement for higher doses of corrosion inhibitor. *Corrosion inhibitors are not required with Arcasolve™.*

The toxicity of corrosion inhibitors presents problems when disposing of spent HCl based acidizing fluid.. *Arcasolve™ presents minimal chemical safety/toxicity problems to well process operators and is recognized to be a "green" product.*

It is possible to use Arcasolve for drilling damage removal from horizontal wells by introducing Arcasolve™ through the drill string following drilling operations. *Use of coiled tubing, commonly used to place HCl is not needed with Arcasolve™.*

There is no requirement for additives to be added to Arcasolve™ to retard the rate of reaction. In particular high viscosity additives are not required, which present problems in applications such as fracture acidizing. *Clean up following Arcasolve™ treatments is straightforward.*

7.b. Comparison to Emulsified HCl

Emulsified HCl involves the use of both organic solvents and HCl. Both are hazardous before and after mixing. The emulsion may not give a good distribution of acid downhole.

The use of certain organic solvents in gas and water injection wells may reduce the gas or water relative permeability and permanently reduce well production. The use of a water based acidizing system with good penetration would be preferred for such wells allowing much easier control over the wetting characteristics of the formation.

Use of oil-external emulsified acids may be limited by the increased frictional resistance to flow of these fluids down well tubulars.

Arcasolve™ is lower hazard and does not suffer from injectivity or wettability problems.

7.c. Comparison to Acetic Acid

Although acetic acid reacts more slowly than HCl, the reaction is still sufficiently rapid to give the problems summarized in section 2. In contrast, generation of acetic acid *in-situ* using Arcasolve™ allows acid to be delivered much deeper into the formation and better placement of acid along extended well-bores. Arcasolve is therefore more effective, and offers a much higher degree of control of acidizing than acid formulations based on acetic acid or other organic acids.

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