Effective water-based drill-in fluid filter cake cleanup by treatment fluids containing organic acid precursors

A discussion of laboratory and field experience
Generation of organic acid in-situ from acid precursors is now firmly established as an effective acidizing and filter cake treatment method.

This paper discusses the basis of in-situ organic acid generation and its applicability to the cleanup of water-based drill-in fluid filter cake. The literature on field use and laboratory evaluations is referenced and lessons learnt are highlighted.

The importance of filter cake cleanup; why cleanup is required

Drill-in fluids (DIFs) are designed to deposit a filter cake during the drilling of oil, gas or water wells. DIFs are relatively clean compared to conventional mud systems and are designed to minimise the effects of drilling fluid damage when drilling through the pay zone. They are typically formulated to deposit a high quality, relatively impermeable filter cake. This minimises fluid loss and seals off the reservoir from the wellbore.

The filter cake acts as a barrier to production. In order to maximise the production rate and net present value (NPV) of the well, the filter cake needs to be removed as uniformly as possible from the whole of the production interval.

In vertical wells in high permeability formations, high draw-down may be sufficient to lift the filter cake off the formation face and achieve a reasonable level of cleanup without using chemicals such as filter cake breakers. However, uniform, effective cleanup can be very hard to achieve in low permeability or variable permeability formations.

Uniform cleanup is even more difficult to achieve in horizontal wells. Horizontal wells are increasingly widespread due to their high production potential and ability to access remote reserves. Their use can also reduce the number of wells required to develop prospects and significantly reduce the potential to avoid water or gas coning. However, horizontal wells have lower draw-down than vertical wells. This makes uniform, effective filter cake removal even more important.

Heterogeneous reservoir characteristics across the horizontal openhole can result in variable draw-down making cleanup uneven. There may also be variation in the extent of initial damage across the production interval. Typically, the part of the wellbore that has been exposed to the drill-in fluid for the longest period is the most damaged.

If left in place, the filter cake can significantly reduce the production rate of a well, cause a poor production profile and reduce the efficiency of the completion. Production complications such as gas or water coning can also arise.

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Use of acid for cleanup of filter cake

Historically, acid, particularly hydrochloric acid (HCl) has been used to treat drilling fluid damage. Acid treatments are suitable where the well has been drilled with a DIF containing an acid-soluble material such as calcium carbonate or has been drilled into a carbonate formation so the DIF contains carbonate formation fines.

HCl acidizing can give good results in wells with short production intervals. When used to treat longer producing intervals, HCl is typically used in conjunction with various diversion techniques or coiled tubing (CT).

However, the very fast reaction rate of HCl can significantly limit the zonal coverage achieved by HCl treatments, even when placed by CT. When using HCl it is difficult to achieve uniform damage removal over long openhole horizontal producing intervals which can result in disappointing well productivity. If the wellbore is near water bearing zones, there is a significant risk that using HCl may “wormhole” through to water bearing zones and significantly increase water production.

In addition it stated that another major concern was corrosion of sand control screens because of ineffective displacement of acids and low spots/holdup in well trajectory.

Other work has concluded that “Slow reacting breakers such as enzymes and oxidizers, should be preferred to remove the polymeric components of water-based RDF filter cakes” and “when removal of bridging agents such as CaCO3 is necessary, two-step treatments (e.g. enzyme or oxidizer soak followed by acid) are considered ineffective unless acid injection is done through a jetting or a cup tool.”

In addition to its undesirable fast reaction rate, use of HCl poses significant health and safety risks as well as corrosion and environmental concerns.

The oil and gas industry has recognised that more uniform placement of acid can be achieved if the reaction of the acid is “retarded” in some way, for example by emulsifying the aqueous acid solutions in oil (or solvents such as kerosene or diesel fuel) to produce an emulsion which is slower reacting, dissolving the acids in a non-aqueous solvent, chemically retarding the system (for example through the use of oil-wetting surfactants) or gelling the acid.

A joint industry study relating to screen completions stated that “Field experience has established and laboratory experiments have supported that rapid reacting acids and particularly HCl cannot provide uniform filter-cake removal.”

The importance of filter cake cleanup in sand control completions has been recognised. A joint industry study concluded that “Regardless of the completion technique, filter cake cleanup should be considered essential for high productivities, particularly in premium/prepacked stand alone screen (SAS) and gravel packed completions. Not performing a filter cake cleanup treatment, in combination with incomplete packing, can lead to hot spots and eventual screen failure.”
Use of in-situ acid production for filter cake cleanup

In the 1990s, Cleansorb introduced an in-situ acidizing process that was not dependent on slowing up the rate of reaction of an acid that was already present but was instead based on generation of an organic acid at a controlled rate in an aqueous solution.

This first generation system was based on a combination of (a) an environmentally friendly and water-soluble acid precursor with (b) an enzyme able to break down the precursor to release the organic acid.\(^3,4\)

Independent tests of the first generation system demonstrated that it was effective against many water-based mud filter cakes. This in-situ acidizing technique also significantly increased the permeability of San Andres dolomite rock cores with increases in permeability of 100% to 340% observed in independent tests.

Other tests\(^3\) directly evaluated the zonal coverage achieved by in-situ acid generation compared with HCl. Cores were mounted in series and damaged with water-based polymer mud. Either HCl or acid precursor treatment fluid was flowed across the core faces, passing across the damaged face of the first core before it could reach the face of the second core.

The HCl rapidly broke through the first core, limiting the amount of acid reaching the second core. Using in-situ acid generation based on the use of acid precursors, with a sufficient soak time, significant increases in permeability were observed in both cores.

The results indicated that in-situ acid generation showed greater potential than HCl for complete zonal coverage of drilling damage caused by water-based muds across extended horizontal or directional intervals.

Although many different organic acid precursors could potentially be used for generating organic acid in-situ, it is desirable that the precursor should be reasonably soluble in water or oilfield brines and also generates an organic acid that reacts with acid soluble material such as calcium carbonate to produce a salt with good solubility.

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Acid precursors that generate formic acid, acetic acid or lactic acid are probably the most useful. They are now in widespread use as components of filter cake breaking treatment formulations.

In general, formic acid precursors such as Cleansorb’s Acidgen FG and Acidgen FG2 have been shown to be suited to use at lower temperatures (approximately 20-90° C) and acetic or lactic acid precursors such as Acidgen HA or Acidgen LG are more suited to use at higher temperatures (approximately 90-160° C). Recently, Cleansorb has developed some novel acid precursor systems that can be used in very low temperature formations (6-20° C).

Some workers consider that the use of precursors of low pKa organic acids such as formic or lactic acid are to be preferred to precursors of higher pKa organic acids such as acetic, as the former are “stronger” acids. However, complete filter cake breaking can be achieved using acetic acid precursors and these compounds are highly acceptable from an environmental point of view. One argument that has been advanced in relation to systems that generate acetic acid arises from the knowledge that in conventional acidizing with acetic acid there is a buildup of carbon dioxide and that an equilibrium is established which prevents all of the acetic acid from reacting. Although this may be true in an effectively closed system on the relatively short timescale of conventional acidizing, field data (based on measuring the amount of calcium carbonate dissolved during acidizing with acetic acid precursors over several days at about 100° C) has indicated that not only is there full conversion of acetic acid precursor to acetic acid and full reaction with carbonate, but the amount of carbonate dissolved was consistent with further dissolution of carbonate as a result of carbonic acid formation. Twice as much calcium carbonate was observed to have been dissolved compared to what would have been dissolved by full reaction of the acetic acid produced by 100% conversion of the acetic acid precursor to acetic acid.

The rate of acid generation from acid precursors can be increased using enzyme or non-enzyme catalysts. So, for example, in low temperature formations below 30° C use of a formic acid precursor alone may require a 6 day shut-in to allow acid production. Incorporating a suitable enzyme to convert the acid precursor to formic acid can reduce the required shut-in time to 2 days.

As well as providing excellent zonal coverage, acidizing approaches based on the in-situ generation of organic acids deliver a number of additional advantages over HCl, providing significant health, safety and environmental benefits.

Whilst in-situ generation of organic acids is effective for dissolving the acid-soluble components of filter cakes, it is also highly desirable to degrade any polymers present in the filter cakes.

The importance of breaking polymers in filter cakes

Water-based drill-in fluids are generally comprised of water or brine plus weighting and fluid loss additives such as ground calcium carbonate, barite, starch, cellulose (typically polyanionic cellulose, PAC) and viscosifying polymers such as xanthan.

Polymers and some particulate material may enter the formation during the formation of a filter cake on the wellbore face. A study of polymer loss in filter cake formation41 states that “xanthan gum molecules will freely enter formations having a permeability greater than 50 to 100 mD, but are filtered out at lower permeabilities.” The same paper indicates that the extent of polymer loss to the formation also varies with the type of polymer and the type of particulates present in the fluid that is being filtered out on the rock formation face.

The process of formation of the filter cake results in the components of the drill-in fluid being concentrated into the filter cake. Locally there is a high concentration of polymers and particulate materials such as calcium carbonate in the filter cake.

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As an example of the degree of concentration of polymers from a treatment fluid during filter cake formation, it has been reported that filter cakes produced during fracturing can contain up to about 48% by weight of polysaccharide versus about 4% by weight in the fracturing fluid.

Generally both an external filter cake and an internal filter cake are formed during drilling. An external filter cake results in wellbore narrowing. The internal filter cake is formed as a result of invasion of the rock matrix by particles smaller than the pore bridging size.

A study of enzyme polymer breakers found that starch or polyanionic cellulose (PAC) in drill-in fluids appeared to be solely responsible for bonding of particles in the filter cake. Disruption of starch/xanthan filter cakes could be achieved using starch breaking enzymes and disruption of PAC/xanthan filter cakes could be achieved using cellulose breaking enzymes. Filter cake destruction could be achieved without affecting the xanthan viscosifier. Fortunately, enzymes are available which are highly effective for the degradation of starches and celluloses. However, only partial degradation of xanthan can be achieved using enzymes.

Although polymer breaking enzymes may effectively disrupt the bonding of filter cake particulates, using enzymes alone has no effect on calcium carbonate. This needs to be removed using an appropriate solubilising treatment, such as acidizing.

In cases where enzymes are used to treat a filter cake and calcium carbonate must also be removed, it was stated that a postflush with an acid is also required.

Removal of polymers in order to facilitate acidizing may be necessary. The presence of polymers can potentially interfere with acidizing. Coating of solid particles such as calcium carbonate with polymer can prevent their reaction and removal with acid.

The need to both degrade polymers and dissolve calcium carbonate to obtain a clean, productive well has been borne out by field experience. When treating a series of 31 offshore wells using a specific starch breaking enzyme, it was concluded that “optimal production performance can only be achieved when specific enzyme breaker treatments are followed by acid stimulation.” In this case, because enzymes are not compatible with conventional acids such as HCl, it was necessary to perform a two-stage treatment, with an enzyme soak followed by a separate acid treatment.

It is apparent from the above that to obtain complete cleanup of filter cakes produced from water-based muds it is highly desirable and probably necessary to make a dual attack on the filter cake, to (1) degrade polymers present in the filter cake and (2) dissolve the calcium carbonate.

Oxidizing agents or enzymes have both been widely used to break down polymer in filter cakes. Such oxidizing agents or enzymes are generally referred to as polymer breakers. However, oxidizing agents or enzymes do not dissolve calcium carbonate.

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Polymer breaking cannot be achieved by placing enzymes into a conventional acid such as HCl as the enzymes are normally immediately inactivated at the very low pH of the acid solution.

An alternative to the use of enzymes to degrade polymers is the use of oxidizing agents. However, oxidizing agents, in common with enzymes, are generally not compatible with HCl. There are other issues associated with using oxidizing agents, such as the possibility of generating toxic gases if added to certain brines and their possible involvement in increasing corrosion rates. For example, combining acids and hypochlorite oxidizing agents generates chlorine gas, which is undesirable on health and safety grounds. Oxidizers are also less specific polymer breakers than enzymes.

It is therefore not possible to achieve a dual attack on filter cakes (degrading polymers and dissolving calcium carbonate) in a single treatment fluid, when using treatment processes based on conventional acids such as HCl. Sequential treatments with two different fluids are needed.

In-situ acidizing formulations can achieve a dual attack on the polymeric and carbonate components of filter cakes in a single treatment fluid

As indicated above, it is highly desirable to remove completely both the carbonate and polymer components of the filter cake.

In-situ acidizing formulations can achieve a dual attack on the polymeric and carbonate components of filter cakes in a single treatment fluid

Normally enzyme polymer breakers are incorporated, although oxidizing breakers may be used instead of enzymes.

Second generation systems do not require use of an enzyme or non-enzyme catalyst to increase the rate of acid generation, although this may sometimes still be used in certain situations, such as acidizing of low temperature formations.

When using precursors of formic or lactic acid, which are stronger acids (i.e. lower pKa) than acetic acid, it has been reported that polymers can be directly degraded by the stronger organic acids formed.15 It has been separately reported16,17 that low pKa organic acids produced from acid precursors can degrade starch at temperatures above 70° C.

However it is not clear if polymer (starch) degradation has been demonstrated in the presence of calcium carbonate. The primary function of the organic acid produced from an acid precursor is to dissolve calcium carbonate. As the carbonate is dissolved by formic or lactic acid, an increasing amount of calcium formate or calcium lactate is formed. This forms a buffer system with the low amount of free organic acid in the system, increasing the pH of the system. Our own investigations have observed that when treating carbonate polymer filter cakes with formulations containing low pKa organic acid precursors only (i.e. with no starch breaking enzyme present) starch can still be detected in filter cake residues even after all of the carbonate has been dissolved. Whilst it appears likely that starch is fully degraded above 70° C in the absence of calcium carbonate, it is questionable if starch is adequately degraded at the higher pH values that prevail in the presence of calcium carbonate.

Interestingly, in filter cake treatment systems based on precursors of sulfonic acids9 which have a much lower pKa than even formic or lactic acid, much better regained permeability was obtained when acid generation was combined with the use of an enzyme polymer breaker.10 This suggests that using enzymes to degrade polymers is more effective than relying solely on a low pH arising from generating a low pKa acid in-situ.

Cleansorb has developed patented second generation in-situ acidizing fluids for filter cake treatment.13,14 These allow polymer breakers to be combined with acid precursors in a single treatment fluid, resulting in a dual attack on the polymers and the carbonate present in the filter cake.
Typical filter cake treatment formulations based on organic acid precursors

Filter cake breaking formulations based on organic acid precursors are tailored to the requirements of the treatment, taking into account the bottomhole static temperature, desired break time and DIF composition.

Typically, formulations containing 10% to 20% acid precursor by weight produce enough acid to dissolve the calcium carbonate present in most carbonate polymer DIF filter cakes. The formulation is made up in a suitable brine to give the fluid the required final specific gravity. A little sodium bicarbonate may be added to neutralise the small amount of free acid present in acid precursors from the manufacturing process. Alternatively, a conjugate base of the organic acid being generated may be used to increase the pH. The maximum amount of free acid is typically around 0.5% of the acid precursor concentrate by weight.

Depending on the requirements of the treatment, other components may include an enzyme to accelerate the rate of acid production from the acid precursor, polymer breaking enzymes (optionally with a buffer) or a suitable oxidizing breaker.

In designing treatment formulations, suitable consideration should be given to any requirements for shale inhibition or hydrate suppression.

Treatment timescales may vary. Many filter cake treatments are conducted over a 1 to 3 day timescale, but in some cases, treatments on a timescale of hours are desirable.

At the other end of the spectrum, some wells are suspended post-completion for many months before being put on production or injection, allowing treatment over weeks rather than days. Particularly when shutting-in for prolonged periods, consideration may be given to including a suitable corrosion inhibitor.

Use of acid precursors for effective filter cake removal – laboratory evaluation

The effectiveness of treatment formulations based on organic acid precursors for water-based DIF filter cake removal has now been demonstrated in numerous laboratory studies where filter cakes have been generated on either ceramic discs or core material. Most work has used precursors of formic, acetic or lactic acid.

Effective formulations consisting of either acid precursor only,4,12,18-24 acid precursor plus an enzyme (to increase the rate of acid generation),3,13,14,25 acid precursor plus polymer breaking enzyme(s)14,25,26 or acid precursor plus oxidizing agent27-29 have all been reported. The effectiveness of the cleanup achieved has been evidenced by excellent regained permeabilities.

Where suitable polymer breakers, such as starch breaking enzymes, cellulose breaking enzymes or oxidizing agents are also incorporated into the treatment formulations, laboratory studies have shown that the polymeric components of the filter cake are also degraded. In the large majority of cases with most drill-in fluids, enzyme polymer breakers are highly effective for polymer breaking and breaking of either starch or cellulose which are the most important polymeric components of filter cakes to degrade.6 As xanthan is only partially degraded using enzymes, use of oxidizing breakers for xanthan breaking may be indicated where xanthan is identified as a cause of residual formation damage, after dissolving calcium carbonate and degrading starch or cellulose.

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In relation to starch breaking using enzymes, it is highly desirable to incorporate a suitable buffer to ensure that pH conditions remain suitable for the operation of the enzyme. If the pH falls too low, starch breaking enzymes become inactive. Use of a buffer is particularly important when using acid precursors of low pKa acids such as formic acid.

In some cases when evaluating possible breaker formulations against filter cakes made using field muds of unknown polymer composition, standard enzyme polymer breakers have sometimes been observed to be ineffective (unpublished results). The presence of the polymers has also been observed to prevent substantive carbonate dissolution by acid produced from acid precursors. In those cases where standard polymer breaking enzymes are not effective, use of a suitable oxidizing agent, if compatible with the brine, has generally been demonstrated to result in polymer degradation and high regained permeability.

It is desirable to confirm the compatibility of a proposed treatment formulation with the makeup brine. Generally, the treatment formulation will be based on the completion brine. The solubility of the acid precursor in the brine at the desired density should be confirmed. Also, the solubility of any “acid-generating” enzymes, active against the acid precursors, or “polymer-breaking enzymes” active against polymers in the filter cakes should be checked.

The solubility of enzymes can vary depending on the brine concentration, type of brine, pH, concentration of solvents and temperature. Under the wrong combination of conditions, individual enzymes may be precipitated out of solution. Even though enzymes are used at relatively low concentrations (typically 0.05% to 1% v/v of a liquid preparation) it is desirable to avoid this. Enzymes resistant to precipitation under typical treatment conditions should be used in field applications.

If using oxidizing agents as polymer breakers, it is essential to consider their compatibility with brines. For example, most oxidizing breakers are ineffective in formate brines. A number of oxidizing agents may generate chlorine in chloride brines or bromine in bromide brines which is highly undesirable for health and safety reasons. Use of oxidizing agents may also result in higher corrosion rates.

In addition to being highly effective for removal of filter cakes, treatment formulations based on acid precursors are typically low viscosity with a low surface tension and/or interfacial tension.

**This makes the application of in-situ acid generation particularly suitable for treatment of gas wells.**

For example, in a study of the use of acetic acid precursor on the removal of filter cake from gas wells\textsuperscript{18,19} it was noted that if aqueous treatment fluids enter the near wellbore area, capillary forces can trap the aqueous phase. Low surface tension values are needed to reduce the capillary forces and allow fluid to be readily removed from the formation.

As a by-product of in-situ acid generation, an organic acid and a relatively short chain alcohol are generated. As both tend to reduce surface tension, this permits faster removal of fluid from the formation, leading the study\textsuperscript{18} to conclude that the low surface tension of acetic acid precursor and the resulting spent solution was relatively low and would reduce the time needed to lift fluids from the formation in which the gas well was drilled.

A subsequent study\textsuperscript{26} showed that formic acid precursors also generated spent solutions with a low surface tension.

When using conventional acidizing it is common to viscosify treatment fluids to try to improve zonal coverage. The removal of high viscosity fluids can cause particular problems when treating gas wells, with the time required to achieve cleanup increasing significantly as the 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 fluid will have been produced after 400 days of production.\textsuperscript{32}

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In addition to the effective removal of filter cakes, treatment fluids containing acid precursors can give an additional benefit in treating carbonate formations. Drilling into carbonate formations has been reported to result in a very low permeability crush zone behind the filter cake.\textsuperscript{16,24} \textbf{In-situ acid production within the near wellbore formation can remediate such crush zones, by restoring matrix permeability resulting in improved well productivity.}\textsuperscript{24}

**Fig 4.** Cleanup of filter cake by treatment formulation based on organic acid precursors

Testing filter cakes produced from lab drill-in fluids can give good comparative data on the relative performance of different breakers against the DIF filter cake, and an indication of minimum break time, but it should be borne in mind that field DIF will include drill solids which could affect the filter cake composition and breakthrough time. Filter cakes made on ceramic discs in HPHT cells, generally made under static conditions, are likely to differ from those made under dynamic conditions in field situations. Filter cake produced in the lab may not behave the same as that produced under field conditions resulting, for example, in different breakthrough times under lab test and field conditions.

The presence of drill solids in a DIF appears to have the potential to increase the break time of a filter cake. It has been observed that in laboratory tests of a given breaker formulation, breaking filter cakes formed from field DIFs can take longer than breaking those formed from lab DIFs. Similarly, breaking of filter cakes formed from lab DIFs containing simulated drill solids can take longer than breaking those formed from lab DIFs alone. For example, adding Hymod Prima clay at 20 kg/m\textsuperscript{3} to a DIF increased the time taken for filter cake breakthrough from 1 hour to 27 hours.\textsuperscript{23} One simple explanation is that the filter cakes are more likely to be thicker when particles that are sub-optimal for bridging are also present.\textsuperscript{33}

Similarly, viscosifying the treatment formulation with a suitable viscosifying agent can typically double the time taken to break through a filter cake.

In some cases when using brines at near saturation, dissolution of calcium carbonate with organic acid generated from acid precursors can lead to the deposition of crystals of calcium salts of the organic acid as the solubility limit is exceeded. For example, calcium formate may be deposited in dense formate brines when using formic acid precursors.

Consideration needs to be given to the possibility of the deposition of calcium salts in dense brines at the treatment design stage.

Some technical solutions to avoid deposition have been proposed.\textsuperscript{34} For example the use of certain chelating agents or surfactants to increase solubility or prevent crystal seeding of calcium formate in dense formate brines. Salt deposition may be avoided by switching to another brine.

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Summary of lessons learnt – lab evaluations of treatment fluids based on acid precursors

- Excellent cleanup of filter cakes can be obtained, with both carbonate and polymer components of filter cakes dissolved or degraded
- The type and amount of acid precursor needs to be selected according to the formation temperature, type of brine, desired breakthrough/cleanup time
- Formic acid precursors are generally better suited to lower formation temperatures
- Acetic acid precursors and lactic acid precursors are generally better suited to higher formation temperatures
- The rate of acid generation can be increased using enzyme or non-enzyme catalysts
- Solubility of the products of in-situ acidizing may be limited in some concentrated brines although some technical solutions are available to address this problem
- The surface tension of spent solutions arising from the use of acid precursors is generally low enough to assist in the cleanup of gas wells
- When using polymer breaking enzymes in the formulation, it is desirable to confirm that these remain in solution in the spent treatment fluid at BHST. Suitable polymer breaking enzymes have been developed by Cleansorb
- Acid precursors can be effective in increasing the permeability of carbonate rock behind the filter cake, including remediation of very low permeability crush zones by matrix stimulation
- Breakthrough times in lab evaluations are indicative of minimum break times but it needs to be appreciated that filter cakes deposited in the field may give a different response
- Breakthrough time in laboratory tests have been reported to be increased by the inclusion of simulated drill solids in the drill-in fluid
- Viscosifying the treatment fluid can increase the time taken to breakthrough the DIF filter cake

Use of acid precursors for effective filter cake removal – field use

Treatment formulations based on acid precursors have been used to treat successfully filter cakes in many different types of well in both sandstone and carbonate formations.

Situations where they have been used include:

- Horizontal openhole
- Horizontal openhole with stand alone screens
- Horizontal openhole with expandable screens
- Horizontal openhole gravel pack
- Water injection wells
- Oil producers
- Gas producers
- Multilateral completions

Treatments of new wells and remedial treatments of older wells have been carried out.

Ideally, filter cake damage is treated before the well has been put on production. This is because after drilling there is an intact filter cake lining the openhole section which regulates leak off of the treatment fluid as it is placed. This assists in filling the openhole section to be treated. Treatment fluids based on acid precursors have an initially low reactivity and do not react quickly with weak spots in the filter cake in the same way as reactive treatment fluids such as hydrochloric acid. This avoids the leak off problems associated with reactive treatment fluids.

It is also possible to treat filter cake in gravel packs. The treatment fluid may be used as the carrier fluid for the gravel pack, and/or placed inside the screens after gravel packing.
Treatment fluids based on acid precursors have also been used to stimulate successfully openhole wells that have already been on production but which were not cleaned up properly in the first place.

Placement of the treatment fluid will be dealt with by a separate white paper. In general terms, the ideal time to use filter cake cleanup treatments is on new wells, where the presence of an intact filter cake actually assists in the placement of the treatment fluid, improving the eventual zonal coverage that can be achieved.

A number of different types of formulations containing acid precursors have been used in field treatments. These include formulations consisted of acid precursor only, acid precursor plus enzyme (to increase the rate of acid generation), acid precursor plus polymer breaking enzyme(s), or acid precursor plus oxidizing agent.

A major concern in conventional acidizing treatments is the potential for unwanted stimulation of water. In-situ acidizing has been used for remedial filter cake treatments in horizontal wells in field margins where previous conventional acidizing is known to have resulted in massive increases in water production. Wormholing by conventional acid treatments resulted in extensive communication with water bearing zones in relative close proximity to the production wellbore.

In remedial treatment of horizontal wells using bullheaded in-situ acidizing fluid, reductions in GOR have been observed, suggesting that gas coning has been reduced.

Effective filter cake cleanup has been achieved at temperatures ranging between about 20° C and 150° C. Formulations need to be tailored to the temperature as well as the brine and proposed shut-in period.

Using in-situ acidizing, increased oil production has been achieved in a number of fields without stimulating water production.
Significant increases in the pore sizes of limestone cores treated with in-situ acidizing fluid were also observed. It was considered that the ability of the delayed-release acid system to match or outperform significantly “stronger” treatments by hydrochloric acid is due to:

- The greater ability of the delayed-release acid system to treat more of the entire length of the openhole
- Acid release into the rock matrix, leading to an increase in permeability and the size of pore throats

Acidizing of the rock matrix behind the filter cake was believed to remediate a “low permeability crush zone.”

The low corrosion rate of treatment formulations may allow ESPs, expensive completion “jewellery” etc to remain downhole during treatment. For example in one treatment, fluid was bullheaded through a bypass in an ESP downhole which avoided having to pull the ESP at a significant cost.

It has been reported that an average of 88% higher production was obtained from two openhole horizontal wells treated with an organic acid precursor compared to two wells treated with hydrochloric acid. This was despite the organic acid precursor treatment dissolving only two thirds as much calcium carbonate per linear metre of hole as the HCl treatment.

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Regulatory status of organic acid precursors

Acetic acid precursors are generally available for use in all geographical areas. Some formic acid precursors are not currently available for use in North America and Australia.

Some formic acid and lactic acid precursors are now regulated for transportation.

In the North Sea, Cleansorb’s acetic acid precursor (Acidgen HA) and formic acid precursor (Acidgen FG) are both rated gold band.

Some Cleansorb acid precursors break down to solely PLONOR products.

Potential for corrosion

When using acid precursor to treat water-based drill-in fluid filter cakes containing carbonate, only low concentrations of organic acid are present in the treatment fluid at any moment in time. This is because as the organic acid is generated, it reacts with carbonate present in the filter cake, resulting in the production of a soluble calcium salt. The increase in conjugate base concentration (formate or acetate respectively, when formic or acetic acid precursors are used) results in the formation of a buffer system, keeping the pH higher than it would be if acid only was present, reducing the possibility of high corrosion rates.

However, in designing treatments, it is prudent to consider the situation where acid might be produced in a portion of the treatment fluid that is not in contact with carbonate. Corrosion rates will vary according to the temperature, completion brine, type and concentration of acid produced from acid precursors, presence of carbonate or buffer and duration of exposure. Tests have indicated that acetic and formic acid precursors, in the absence of carbonate or buffer, generally exhibit low corrosion rates against 316L stainless steel, Superduplex 2507 and Nickel Alloy 825 at temperatures up to at least 100° C. However, higher corrosion rates have been observed against L80-13Cr steel and J55 or K55 alloy. To bring corrosion rates against 13Cr down to an acceptable level one very simple and effective solution used in the field when treating filter cake with an acetic acid precursor was to include 2% acetate buffer in the treatment fluid. The same study confirmed that corrosion rates against other alloys present in the completion (Inconel 825 and 316L) were negligible. Where corrosion rates are of concern, corrosion inhibitors known to be compatible with organic acids may also be used.

Benefits of using acid precursors for filter cake treatment

- Dissolves carbonate in filter cakes (not achieved with polymer breaking enzymes)
- Minimises skin
- Maximises production rate and NPV of well
- Non-acidic when placed
  - Allows even distribution of fluid across long sections
  - Minimal leak off during pumping
- Generally low corrosivity to screens, packers and tubulars (corrosion inhibitors not usually required)
- Produces acid evenly along the whole of even a very long horizontal wellbore, producing uniform damage removal and stimulation
- Low hazard
- Low environmental impact
- Lower fluid volumes typically needed than for common cleanup methods using reactive acids such as HCl
- Only requires low power pumping – pumping at high rates and pressures is not needed, further reducing hazards compared to e.g. HCl
- Polymer breaking enzymes may be included in the formulation
- Can be placed in the wellbore via the drillstring during completion
- Can be used as carrier fluid in a gravel pack
# References

1. SPE 85504  
2. SPE 50673  
3. SPE 30123  
4. SPE 50621  
5. SPE 21497  
6. SPE 50709  
7. SPE 27393  
8. SPE 65405  
10. SPE 147480  
11. AADE 01-NC-HO-50  
12. SPE 58732  
13. SPE 68911  
14. SPE 94551  
16. SPE 122327  
17. 15th Bergen SPE conference – April 2008. Recent Advances in the Use of Neutral Organic Acid Precursors in the Breakdown of Water-based and Oil-based Filter Cakes; Productivity and Injectivity Improvements in Limestone and Sandstone Reservoirs.  
18. SPE 96965  
20. SPE 99799  
21. SPE 103846  
22. SPE 151073  
23. SPE 151824  
24. SPE 163344  
25. SPE 144089  
26. SPE 107537  
27. SPE 101181  
28. SPE 101237  
29. SPE 111635  
30. SPE 109754  
31. Unpublished results, onshore Europe and offshore Middle East  
33. AADE-06-DF-HO-16  
34. US 2013/0213659 A1  
35. EXPL-3-EL-211  
36. SPE 98562  
37. SPE/IADC 101964  
38. Halliburton case history H09425 08/12 Statoil N. Sea  
39. SPE 112292  
40. SPE 98164  
41. SPE 39461  
42. SPE 161721  
43. SPE 151683  

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