Faced with poor production from a high-permeability reservoir, an operator’s first thought is a matrix treatment. This commonly involves pumping acid into the near-wellbore region to dissolve formation damage and create new pathways for production. This article reviews the state of the art of matrix acidizing and discusses how technical breakthroughs are helping optimize matrix acid jobs.

The simple aim of matrix acidizing is to improve production—reduce skin in reservoir engineer parlance—by dissolving formation damage or creating new pathways within several inches to a foot or two around the borehole. This is done by pumping treatment fluid at relatively low pressure to avoid fracturing the formation. Compared with high-pressure fracturing, matrix acidizing is a low-volume, low-budget operation.

Matrix acidizing is almost as old as oilwell drilling itself. A Standard Oil patent for acidizing limestone with hydrochloric acid [HCl] dates from 1896, and the technique was first used a year earlier by the Ohio Oil Company. Reportedly, oil wells increased in production three times, and gas wells four times. Unfortunately there was a snag—the acid severely corroded the well casing. The technique declined in popularity and lay dormant for about 30 years.

Then in 1931, Dr. John Grebe of the Dow Chemical Company discovered that arsenic inhibited the action of HCl on metal. The following year, the Michigan-based Pure Oil Company requested assistance from Dow Chemical Company to pump 500 gallons of HCl into a limestone producer using arsenic as an inhibitor. The previously dead well produced 16 barrels of oil per day, and interest in acidizing was reborn. Dow formed a subsidiary later called Dowell to handle the new business (next page, top). Three years later, Halliburton Oil Well Cementing Co. also began providing a commercial acidizing service.

Sandstone acidizing with hydrofluoric acid [HF]—hydrochloric acid does not react with silicate minerals—was patented by Standard Oil company in 1933, but experiments in Texas the same year by an independent discoverer of the technique caused plugging of a permeable formation. Commercial use of HF had to wait until 1940, when Dowell hit on the idea of combining it with HCl to reduce the possibility of reaction products precipitating out of solution and plugging the formation. The mixture, called mud acid, was first applied in the Gulf Coast to remove mudcake damage.
For help in preparation of this article, thanks to A. Ayorinde, Ashland Oil Nigeria Ltd, Lagos, Nigeria; Jim Collins, Dowell Schlumberger, Calgary, Alberta, Canada; Harry McLeod Jr, Conoco, Houston, Texas, USA; Arthur Milne, Dowell Schlumberger, Dubai; Carl Montgomery, ARCO Oil and Gas Co., Plano, Texas, USA; Giovanni Paccaloni, AGIP S.p.A., Milan, Italy; and Ray Tibbles, Dowell Schlumberger, Lagos, Nigeria.

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**Chemistry**

Matrix acidizing of carbonates and silicates are worlds apart. Carbonate rocks, comprising predominantly limestone and dolomite, rapidly dissolve in HCl and create reaction products that are readily soluble in water:

\[
CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O
\]

Limestone Hydrochloric acid Calcium Carbon Water
dioxide chloride oxide

\[
CaMg(CO_3)_2 + 4HCl \rightarrow
\]

Dolomite Hydrochloric acid Calcium Magnesium Carbon Water

dioxide chloride chloride dioxide

\[
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\]

Calcium Magnesium Carbon Water

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The rate of dissolution is limited mainly by the speed with which acid can be delivered to the rock surface. This results in rapid generation of irregularly shaped channels, called wormholes (left). The acid increases production by creating bypasses around the damage rather than directly removing it. By comparison, the reaction between HF and sandstones is much slower. Mud acidizing seeks to unblock existing pathways for production by dissolving wellbore damage and minerals filling the interstitial

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pore space, rather than by creating new pathways. The HF reacts mainly with the associated minerals of sandstones, rather than the quartz (right). The acid reactions caused by the associated minerals—clays, feldspars and micas—can create precipitants that may cause plugging. Much of the design of a sandstone acid job is aimed at preventing this (see “HF Reactions in Sandstones,” below).

The usual practice is to preflush the formation with HCl to dissolve associated carbonate minerals. If these were left to react with HF, they would produce calcium fluoride [CaF₂], which precipitates easily. Then the HF-HCl mud acid is injected. Finally, the formation is overflushed with weak HCl, hydrocarbon or ammonium chloride [NH₄Cl]. This pushes reaction products far from the immediate wellbore zone so that if precipitation occurs, production is not too constricted when the well is brought back on line.

Another plugging danger is from fine particles, native to the sandstone, dissolved by the acid but not fully dissolved. To minimize this eventuality, Shell in 1974 proposed lower pumping rates—less likely to dislodge fines—and, more important, a chemical system that did not contain HF explicitly, instead creating it through a chain of reactions within the formation.3 In principle, this allows greater depth of penetration and longer reaction times for maximum dissolution of fines. Since then, several other systems of in-situ generated—or so-called retarded—mud acid systems have been proposed. Recently, Dowell Schlumberger introduced a retarded acid system using fluoboric acid [HBF₄]. This hydrolyzes in water to form HF:\4

\[
\text{HBF}_4 + \text{H}_2\text{O} \leftrightarrow \text{HBF}_3\text{OH} + \text{HF}.
\]

Fluoboric acid Water Hydroxyfluoboric acid Hydrofluoric acid

As HF is spent, dissolving clays and other minerals, it is constantly replenished through hydrolysis from the remaining fluoboric acid. The slow rate of this conversion helps guarantee a retarded action and therefore deeper HF penetration. As a bonus, the fluoboric acid itself reacts with the clays and

HF Reactions in Sandstones

The reaction of hydrofluoric acid [HF] on the pure quartz component of sandstone follows these two equations:

\[
\text{SiO}_2 + 4\text{HF} \leftrightarrow \text{SiF}_4 + 2\text{H}_2\text{O},
\]

Quartz Acid Silicon tetrafluoride and

\[
\text{SiF}_4 + 2\text{F}^- \leftrightarrow \text{SiF}_6^{2-},
\]

Silicon hexafluoride resulting mainly in the silicon hexafluoride anion, SiF₆²⁻.

Reaction with the feldspar, chert, mica and clay components of sandstones also results in this anion, but, in addition, produces a range of aluminum complexes: AlF₂⁺, AlF₃⁺, AlF₅²⁻, AlF₆³⁻.

Constituents of sandstone, all of which are soluble in HCl-HF mud acid systems.

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Silicon hexafluoride also combines with water to produce colloidal silica: 

\[ SiF_6^{2-} + H_2O \leftrightarrow H_4SiO_4 + 4HF + 2F^- . \]

This precipitate has proved controversial. Experts agree that it cannot be avoided, but disagree about whether it damages the formation. Some believe it does, while others argue that it is not a significant problem. Research by Dowell Schlumberger suggests that colloidal silica is formed during acid treatment and may contribute to fines migration issues in sandstone reservoirs.

Nitrogen is used to block high-permeability pathways within the matrix (see “Diverting With Foam,” page 30). The requirements on any diverting agent are stringent. The agent must have limited solubility in the carrying fluid, so it reaches the bottom of the hole intact; it must not react adversely with formation fluids; it must not divert acid. Finally, it must clean up rapidly so as not to impede later production. Ball sealers drop into the rathole as soon as the perforations are drilled, sealing the wellbore to prevent fines from entering the formation. The main technique for avoiding calcium fluoride precipitation is the HCl preflush, designed to remove carbonate material before HF is injected.

Precipitates and their potential to damage the formation remain a fact of life for the matrix acidizer. But their impact can be greatly minimized through the use of an adequate preflush, the correct mud acid formulation, and the avoidance of any salts except ammonium chloride.

\[ Al_3 + 3F^- \leftrightarrow AlF_3, \]
\[ Al_3 + 3OH^- \leftrightarrow Al(OH)_3 . \]

However, these two compounds can generally be avoided through proper design of preflush and mud acid formulation.

Oftentimes, acidizing can produce ferrous and ferric ions, either from dissolving rust in the tubulars or through direct action on iron minerals in the formation. These ions can then produce more precipitates: ferric hydroxide \( \text{Fe(OH)}_3 \) and, in some wells, ferrous sulfide \( \text{FeS} \). Various chelating and reducing agents are employed to minimize the impact of these two compounds.

Lastly, damage can arise through the precipitation of calcium fluoride \( \text{CaF}_2 \), when HF reacts with the carbonate mineralogy of sandstones:

\[ \text{CaCO}_3 + HF \leftrightarrow \text{CaF}_2 + H_2O + CO_2 . \]

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Production improvement in a Nigerian oil well after fluoboric acid treatment. The well was initially acidized with mud acid and produced 850 barrels of liquid per day (BLPD) with a 34% water cut. Production then declined almost to zero, most likely due to fines movement. After fluoboric acid treatment, production rose to 2500 BLPD, obviating the need for further acid treatments. Oil production a year after the treatment was 220 BOPD. (From Ayorinde et al, reference 5, courtesy of Ashland Nigeria.)
Table: Choosing a diversion method for matrix acidizing.

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<td>Yes</td>
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In practice, acid and diverting agents are pumped in alternating stages: first acid, then diverter, then acid, then diverter, and so on. The number of stages depends on the length of zone being treated. Typically, one acid-diverter stage combination is planned for every 15 to 25 ft [5 to 8 m] of formation.

**Diagnosis**

If the principle of matrix acidizing appears straightforward, the practice is a mine field of complex decisions. Service companies offer a vast selection of acid systems and diverters, and few people would design the same job the same way. In addition, matrix acid jobs are low budget, typically between $5000 and $10,000 an operation, so the careful attention given to planning much more expensive acid fracturing treatments is often missing. Matrix acidizing is traditionally carried out using local rules of thumb. Worse, jobs are poorly evaluated.

The question that should always be asked before any other is “Why is the well under-producing?” And then: “Will production increase with matrix acidizing?” Production may be constricted for a reason other than damage around the borehole. The only way to find out is through pressure analysis from the deep formation through to the wellhead, using production history, well tests and analysis of the well’s flowing pressures, such as provided by NODAL analysis.6

The crude maxim that matrix acidizing will benefit any well with positive skin has...
Analyzing causes of poor production in a gas well using NODAL analysis of well pressures, from downhole to wellhead. In each figure, well performance is presented by the intersection of a tubing-intake curve—upward-sloping lines, one for each wellhead pressure—and an inflow-performance curve—downward-sloping lines, one for each skin value.

The top NODAL analysis shows inflow performance assuming the well was perforated at two shots per foot, the bottom analysis assuming 12 shots per foot. The tubing-intake curves are the same in both NODAL figures.

At two shots per foot, decreasing skin with matrix acidizing offers only marginal production improvement. At 12 shots per foot, matrix acidizing will offer substantial production improvement.

Causes of High Skin, Other Than Damage
(from McLeod, reference 7.)

- High liquid/gas ratio in a gas well > 100 bbl/MMscf
- High gas/oil ratio in an oil well > 1000 scf/bbl
- Three-phase production: water, oil and gas
- High-pressure drawdown > 1000 psi
- High flow rate > 20 B/D/ft
- > 5 B/D/shot
- Low perforation shot density < 4 shots per foot
- Well perforated with zero-degree phasing
- Well perforated with through-tubing gun, diameter < 2 in.
- Reservoir pressure > bubblepoint pressure > wellbore pressure

Types of damage and where they can occur. Diagnosing location and type of damage is the key to successful matrix acidizing.

NODAL analysis, which predicts a well’s steady-state production pressures, refines this checklist. For example, by comparing tubing-intake curves—essentially the expected pressure drop in the tubing as a function of production rate—with the well’s inflow-performance curve—expected flow into the well as a function of downhole well pressure—one can readily see if the well completion is restricting flow (top, left). Comparing a NODAL analysis with actual measured pressures also helps pinpoint the location of any damage. Damage does not occur only in the formation surrounding the borehole. It can occur just as easily inside tubing, in a gravel-pack or in a gravel-pack perforation tunnel (above).


Foam, a stable mixture of liquid and gas, has been used as a diverter in sandstone acidizing since 1969. By the usual criteria, it is almost perfect. It is cheap to produce; it does a decent job diverting; it does not interact adversely with the formation and formation fluids; and it cleans up rapidly. Foam is produced by injecting nitrogen into soapy water—typically, nitrogen occupies 55 to 75% of foam volume. The soapy water is a mixture of water and small amount of surfactant, or foamer. Injected downhole, foam penetrates the pore space where the cumulatively viscous effect of the bubbles blocks further entry of the treating fluid.

Foam's only drawback is that with time the bubbles break and diversion ceases. This can be seen in laboratory experiments, in which foam is injected simultaneously through two long sand packs, one with high permeability mimicking a thief zone, the other with low permeability mimicking a damaged zone (above, right). The cores are preflushed and then injected with foam. Then, acid is injected. At first, diversion works fine, with the low-permeability sand pack taking an increasingly greater proportion of the acid. But after about one hour, the foam has broken and the thief zone starts monopolizing the treatment fluid.

Researchers at the Dowell Schlumberger engineering center at Saint-Etienne, France discovered that this breakdown can be postponed by saturating the formation with a preflush of surfactant before injecting the foam and also injecting surfactant with every subsequent stage in the acid process. The surfactant adheres to the rock surface and minimizes adsorption of surfactant contained in foam, preserving the foam. As before, the foam progressively diverts treatment fluid to the damaged zone, but now the diversion holds for at least 100 minutes (next page, top). If necessary, damaged formation can first be cleaned with mutual solvent to remove oil in the near-wellbore region—oil destroys foam—and to ensure the rock surface is water-wet and receptive to the surfactant.

Yet further improvement to foam diversion can be achieved by halting injection for about 10 minutes after foam injection. The diversion of treatment fluid to the damaged sand pack now takes effect almost immediately, rather than almost 50 minutes. It seems that given a 10-minute quiescent period, foam in low-permeability sand prematurely breaks down—scientists are not sure why. The combination of surfactant injection and 10-minute shut-in comprises the new FoamMAT diversion service that has seen successful application in the Gulf of Mexico and Africa (see “Field Case Studies,” below).

The FoamMAT technique also provides excellent blockage of water zones in high water-cut wells. In a laboratory simulation, two sand packs were constructed with the same permeability but saturated with different fluids, water and oil (next page, bottom). The preflush injection of surfactant can be seen to favor, as expected, the water zone. Then foam was injected into both packs. When acid was injected, most went into the oil zone confirming an almost perfect diversion.

<table>
<thead>
<tr>
<th>Field Case Studies</th>
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<tr>
<td><strong>Well type</strong></td>
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<tr>
<td><strong>before</strong></td>
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<tr>
<td>High water-cut oil well</td>
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<tr>
<td></td>
</tr>
<tr>
<td>Gas well</td>
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<tr>
<td></td>
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<tr>
<td>Oil well</td>
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<td></td>
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<tr>
<td>Low-perm gas well</td>
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Improvement in staying power of foam diversion, using a preflush of surfactant and further surfactant injection with the acid (top). Further improvement in foam diversion is obtained by having a shut-in period following foam injection (bottom). During this quiescent period, foam in low-permeability sands breaks down and diversion becomes immediate.

Efficacy of FoamMAT diversion in high water-cut wells, proved in a laboratory experiment using two sand packs of the same permeability, but initially saturated with oil and water, respectively.

Damage Scales, organic deposits and bacteria are three types of damage that can cause havoc anywhere, from the tubing to the gravel pack, to the formation pore space. Scales are mineral deposits that in the lower pressure and temperature of a producing well precipitate out of the formation water, forming a crust on formation rock or tubing. With age, they become harder to remove. The treatment fluid depends on the mineral type, which may be a carbonate deposit, sulfate, chloride, an iron-based mineral, silicate or hydroxide. The key is knowing which type of scale is blocking flow.

Reduced pressure and temperature also cause heavy organic molecules to precipitate out of oil and block production. The main culprits are asphaltenes and paraffinic waxes. Both are dissolved by aromatic solvents. Far more troublesome are sludges that sometimes occur when inorganic acid reacts with certain heavy crudes. There is no known way of removing this type of damage, so care must be taken to avoid it through use of antisludging agents.

Bacteria are most commonly a problem in injection wells, and they can exist in an amazing variety of conditions, with and without oxygen, typically doubling their population every 20 minutes or so. The result is a combination of slimes and assorted amorphous mess that blocks production. An additional reason for cleansing the well of these organisms is to kill the so-called sulfate-reducing bacteria that live off sulfate ions in water either in the well or formation. Sulfate-reducing bacteria produce hydrogen sulfide that readily corrodes tubulars. Bacterial damage can be cleaned with sodium hypochlorite and it is as important to clean surface equipment, whence injection water originates, as it is to clean the well and formation.

Two further types of damage can contribute to blocked flow in gravel pack and formation—silts and clays, and emulsions. Silts and clays, the target of most mud acid jobs and 90% of all matrix treatments, can originate from the mud during drilling and perforating or from the formation when dislodged during production, in which case they are termed fines. When a mud acid system is designed, it is useful to know the silt and clay composition, whatever its origin, since a wrongly composed acid can result in precipitates that block flow even

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more. Emulsions can develop when water and oil mix, for example when water-base mud invades oil-bearing formation. Emulsions are highly viscous and are usually removed using mutual solvents.

The interplay of oil and water in porous rock provides two remaining types of damage occurring only in the formation—wettability change and water block. In their native state, most rocks are water-wet, which is good news for oil production. The water clings to the mineral surfaces leaving the pore space available for hydrocarbon production. Oil-base mud can reverse the situation, rendering the rock surface oil-wet, pushing the water phase into the pores and impeding production. A solution is to inject mutual solvent to remove the oil-wetting phase and then water-wetting surfactants to reestablish the water-wet conditions.

Finally, water block occurs when water-base fluid flushes a hydrocarbon zone so completely that the relative permeability to oil is reduced to zero—this can occur without a wettability change. The solution is again mutual solvents and surfactants, this time to reduce interfacial tension between the fluids, and to give the oil some degree of relative permeability and a chance to move out.

**Design**
Assessing the nature of the damage is difficult because direct evidence is frequently lacking. The engineer must use all available information: the well history, laboratory test data, and experience gained in previous operations in the reservoir. The initial goal, of course, is selecting the treatment fluid. Later, the exact pumping schedule—volumes, rates, number of diverter stages—must be worked out.

Since carbonate acidizing with HCl circumvents damage, the main challenge of fluid selection lies almost entirely with sandstone acidizing where damage must be removed. Laboratory testing on cores and the oil can positively ensure that a given HF-HCl mud acid system will perform as desired—it is particularly recommended when working in a new field. These tests first examine the mineralogy of the rock to help pick the treating fluid. Then, compatibility tests, conducted between treating fluid and the oil, make sure that mixing them produces no emulsion or sludge. Finally, an acid response curve is obtained by injecting the treating fluid into a cleaned core plug, under reservoir conditions of temperature and pressure, and monitoring the resulting change in permeability. The acid response curve indicates how treating fluid affects the rock matrix—the design engineer strives for a healthy permeability increase.

Most treatment fluid selection for sandstone acidizing builds on recommendations established by McLeod in the early 1980s. The choice is between different strengths of the HCl-HF combination and depends on formation permeability, and clay and silt content (below). For example, higher strengths are used for high-permeability rock with low silt and clay content—high strength acid in low-permeability rock can create precipitation and fines problems. Strengths are reduced as temperature increases because the rate of reaction then increases.

McLeod’s criteria have since been expanded by Dowell Schlumberger. Recently, this updated set of rules has been merged with about 100 additional criteria on the risks associated with pumping complex mixtures of fluids into the matrix, and incorporated into a computerized expert system to help stimulation engineers pick the best treatment system. The system actually presents several choices of treating fluid and ranks them according to efficiency. When the engineer chooses, the generically defined fluids are mapped on to the catalog of products offered by the service company.

![Evolution of acid system guidelines for sandstones to maximize damage removal and minimize precipitates. The first guidelines in 1983 consisted of a few rules. These were expanded to more complex tables in 1990. Now, knowledge-based systems incorporate hundreds of rules on fluid choice.](image)

<table>
<thead>
<tr>
<th>Acid Guidelines for Sandstones 1983</th>
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<tr>
<td><strong>Condition</strong></td>
<td><strong>Main Acid</strong></td>
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<td>HCl solubility (&gt; 20%)</td>
<td>Use HCl only</td>
</tr>
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<td>High permeability (&gt;100 md)</td>
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<tr>
<td>High quartz (&gt;80%), low clay (&lt;5%)</td>
<td>12% HCl, 3% HF</td>
</tr>
<tr>
<td>High feldspar (&gt;20%)</td>
<td>13.5% HCl, 1.5% HF</td>
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<tr>
<td>High clay (&gt;10%)</td>
<td>6.5% HCl, 1% HF</td>
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<tr>
<td>High clay (&gt;10%)</td>
<td>6.5% HCl, 1% HF</td>
<td>Sequestered 5% HCl</td>
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</tr>
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</tr>
<tr>
<td>Low clay (&lt;5%)</td>
<td>6% HCl, 1.5% HF</td>
<td>7.5% HCl or 10% acetic acid</td>
<td>High clay (&gt;10%), low silt (&gt;10%)</td>
</tr>
<tr>
<td>High chlorite</td>
<td>3% HCl, 0.5% HF</td>
<td>5% acetic acid</td>
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Five essential steps in designing a matrix acidizing job, as incorporated in the Dowell Schlumberger ProMAT software package. Detail (right) shows breakdown of fluid selection—initial choice of main treating fluid, design of all fluid stages and mapping of generic fluids to service company products.

Pumping Schedule for a Two-Stage Job

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<thead>
<tr>
<th>Step</th>
<th>Fluid</th>
<th>Volume bbl</th>
<th>Flow rate bbl/min</th>
<th>Time min</th>
</tr>
</thead>
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<td>Stage 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Preflush</td>
<td>HCl 15%</td>
<td>17.3</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>Main fluid</td>
<td>RMA 13/3</td>
<td>68.2</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>Overflush</td>
<td>HCl 4%</td>
<td>33.0</td>
<td>2.4</td>
</tr>
<tr>
<td>4</td>
<td>Overflush</td>
<td>HCl 4%</td>
<td>20.7</td>
<td>4.8</td>
</tr>
<tr>
<td>5</td>
<td>Diverter slug</td>
<td>HCl 4%</td>
<td>3.1</td>
<td>4.8</td>
</tr>
<tr>
<td>6</td>
<td>Preflush</td>
<td>J 237A</td>
<td>17.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Stage 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Main fluid</td>
<td>HCl 15%</td>
<td>12.6</td>
<td>4.8</td>
</tr>
<tr>
<td>8</td>
<td>Main fluid</td>
<td>RMA 13/3</td>
<td>55.6</td>
<td>1.1</td>
</tr>
<tr>
<td>9</td>
<td>Overflush</td>
<td>RMA 13/3</td>
<td>53.7</td>
<td>1.1</td>
</tr>
<tr>
<td>10</td>
<td>tubing displ.</td>
<td>NH₄Cl brine 3%</td>
<td>33.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

1. Regular Mud Acid, 13% HCl, 3% HF. 2. Four-micron particulate oil-soluble resin, usable up to 200°F.

A pumping schedule computed with ProMAT software, listing for each stage the fluid, volume, pump rate, and pump time. This schedule can be input to a simulator to predict detailed outcome of the matrix acid job, such as skin improvement.

This fluid selection advisor forms one module of the ProMAT productive matrix treatment system that Dowell Schlumberger recently introduced to improve the sometimes unacceptable results of matrix acidizing (top). The ProMAT system provides computer assistance for every step of well diagnosis, and the design, execution and evaluation of matrix acidizing. The package begins with the previously described NODAL analysis for diagnosing why a well is underproducing, then follows with the expert system for fluid selection.

The third component develops a preliminary pumping schedule to ensure a skin value of zero—how many stages of treating fluid, how many diverting stages, how much to pump in each stage, etc. (above). The fourth component is a detailed simulation of the acidization process. Given a pumping schedule, it provides detailed production rates, payout time, and well completion data.

October 1992

Commentary: Harry McLeod

Harry McLeod, senior engineering professional in the drilling division, production technology department, Conoco Inc. Houston, Texas, USA.

Matrix acidizing is generally successful in a damaged formation so long as the well is properly prepared and only clean fluids enter the perforations during treatment.

In carbonate formations, scale is the most common damage. In sandstone formations, the most common damage occurs during or just after perforating and during subsequent workovers as a result of losing contaminated fluids to the formation.

When wells are not properly evaluated with a combination of NODAL analysis, and either core or drillstem test data, treatments are often unsuccessful because restrictions other than formation damage are present, as discussed in this article. Only in recent years has proper attention been given to well preparation and on-site supervision.

Improvements in Conoco matrix treatment operations have been obtained by either pickling the production tubing or avoiding acid contact with the production string through the use of coiled tubing. The best results are obtained with effective diverting procedures that ensure acid coverage and injection into every damaged perforation. In 1985, Conoco achieved a 95% success ratio in a 37-well treatment program using a complete quality control program and effective diversion. More effective diverter design and improved models of dissolution and precipitation based on rock characterization are still needed, especially in sandstones with less than 50-md permeability and for downhole temperatures above 200°F (93°C).

5. The ProMAT system calls on two software packages: the MatCADE software for design and postjob evaluation, and the MatTIME package for job execution and real-time evaluation.
forecasts of injection flow profiles, of the improvement in skin per zone as the job proceeds and of the overall rate/pressure behavior to be expected during the job. This information either confirms the previously estimated pumping schedule or suggests minor changes to guarantee optimum job performance. The fifth and final module uses the results of the simulation to predict well performance after the operation and therefore the likely payback, the acid test for the operator.

At the heart of both the pumping schedule advisor and simulator are models of how an acidizing job progresses. In most of the details, the advisor’s model is simpler than the simulator’s, and even the simulator model is simple compared with reality. Acidizing physics and chemistry are highly complex and provide active research for oil companies, service companies and universities alike.13 For job design, simple models have the advantage of requiring few input parameters but the disadvantage of cutting too many corners. Complex models may mimic reality better, but they introduce more parameters, some of which may be unmeasurable in the field or even in the laboratory. Whatever their level of sophistication, acidizing models must deal with four processes simultaneously:
- tracking of fluid stages as they are pumped down the tubing, taking into account differing hydrostatic and friction losses
- movement of fluids through the porous formation
- dissolution of damage and/or matrix by acid
- accumulation and effect of diverters.

All four phenomena are interdependent. Diverter placement depends on the injection regime; the injection regime depends on formation permeability; formation permeability depends on acid dissolution; acid dissolution depends on acid availability; acid availability depends on diverter placement; and so on.

The computation proceeds fluid stage by fluid stage (below). The time taken for each stage is subdivided into a series of small time steps and this chain reaction is evaluated for each step. The results after one time step serve as the input to the next. In addition, for the more sophisticated simulation, the formation is split into a mosaic of radially symmetric blocks. At each time step, the evaluation must be performed for all blocks simultaneously. The simulator provides a detailed prediction of how the acid job will progress and the expected improvement in skin and productivity (next page, above). This helps decide the bottom line, which is time to payback.

**Execution and Evaluation**

Sophisticated planning goes only part way to ensuring the success of a matrix acidizing operation. Just as important is job execution and monitoring. In a study of 650 matrix acidizing jobs conducted worldwide for AGIP, stimulation expert Giovanni Paccaloni estimated that 12% were outright failures, and that 73% of these failures were due to poor field practice.14 Just 27% of the failures were caused by incorrect choice of fluids and additives. Success and failure were variously defined depending on the well. Matrix acidizing a previously dry exploration well was judged a success if the operation established enough production to permit a well test and possible evaluation of the reservoir. The success of a production well was more closely aligned with achieving a specific skin improvement. Having identified the likely reason for failure, AGIP

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13. University of Texas:
Dowell Schlumberger:


Shell:
After several decades of field practice, countless lab studies and theoretical investigations, matrix acidizing technology is today one of the most powerful tools available to the oil industry for optimizing production. There is still much room for improvement, however. Reasons are:

- the relatively low operational cost compared to the economic benefits
- the great complexity of the physicochemistry phenomena involved, as yet only partially modeled
- the low attention paid so far to the evaluation and to the understanding of actual field acid response, the evolution of skin with treatment fluid injected
- the lack of exhaustive studies matching lab and field results
- the negligible amount of lab work with radial cores, which may provide skin evolution data that linear cores cannot
- the low attention paid so far to validating acidizing techniques using pressure build-up tests and flowmeter surveys
- the small degree of integration between different disciplines—lab scientist, field engineer, production/petroleum engineer, and academia
- the prevailing attitude to preserve consolidated "rules" based more often on the microscale simulation of reality than on the study of reality, i.e., actual well response.

All of the above are receiving intense attention at AGIP. R&D efforts are directed to improving the success ratio and lowering costs, with the underlying idea that any new technique must be validated with field results. Much attention is given to the interdisciplinary approach, to improved training, and to finalized R&D projects. Three expert systems dealing with matrix acidizing design, formation damage diagnosis and well problem analysis have been recently released to our operating districts. New matrix acidizing technologies, developed in-house, are currently under field test. The laboratory study of skin evolution simulating actual field conditions is one of our major concerns.

**Commentary: Giovanni Paccaloni**

Giovanni Paccaloni, head of production optimization technologies department at AGIP headquarters in Milan, Italy.

*Simulation results showing the difference between one- and two-stage matrix acid jobs on a damaged oil well known to produce from two layers. The one-stage job (left) fails to remove damage from layer 2, which is left with a skin of 10. The two-stage job diverts the second acid stage toward this layer, bringing the skin of the entire well to zero.*

Assuming a $15/barrel price for oil, the payback after 30 days is $330,000 for the one-stage job and $520,000 for the slightly more expensive two-stage job. The properly designed, more complex operation appears a reasonable option.
followed up almost all the failures with a second acid job. This not only resulted in improved production, but also confirmed the failure diagnosis in each case.

Reasons for poor field operation centered on the technique of bullheading, in which acid is pumped into the well, pushing dirt from the tubing and whatever fluids are below the packer, often mud, directly into the formation. Bullheading can be avoided by using coiled tubing to place acid at the exact depth required, bypassing dirt and fluids already in the well. Paccaloni recommends use of coiled tubing whenever possible—its benefit for acidizing horizontal wells has been well documented (see “Horizontal Wells: Bullheading Versus Coiled Tubing,” next page).

What helped AGIP identify and correct the failures, though, was reliable real-time monitoring of each job, particularly the tracking of skin. If skin improves with time, the job is presumably going roughly as planned and is worth continuing. If skin stops improving or gets worse, then it may be time to halt operations. The problem initially was the poor quality of field measurements, traditionally simple pressure charts. Then in 1983, digital field recording of wellhead pressures was introduced. Today, fluid density, injection flow rates, wellhead and annulus pressures are recorded and analyzed at the wellsite (above).

Three methods have been proposed to monitor skin. In 1969, McLeod and Coulter suggested analyzing the transients created before and after treatment fluid injection. The analysis was performed after job execution and therefore not intended to be a real-time technique. In 1979, Paccaloni formulated a method that assumes steady-state flow and ignores the transients, but that provides a continuous estimate of skin in real time. Paccaloni used this method to successfully analyze causes of failure in his survey of AGIP matrix jobs.

The key issue in matrix acidizing horizontal wells is acid placement, since both damaged and thief zones can be hundreds of feet long. The two techniques used are bullheading and coiled-tubing placement.

Acidizing horizontal wells by bullheading follows conventional practice, with alternating stages of acid and diverter. Coiled tubing, on the other hand, allows accurate placement of diverter into thief zones before acid is pumped—thief zones can be identified from production logs, Formation MicroScanner images or mud logs. After the thief zones have been treated by positioning the coiled tubing opposite them and injecting diverter, the coiled tubing is run to total depth and gradually withdrawn as acid is pumped. Simultaneous withdrawal and injection provides the most even coverage. If inadequate data are available to identify thief zones, acid and diverter stages can be alternated as the coiled tubing is withdrawn.

Simulations illustrate the effectiveness of the coiled-tubing technique over bullheading. The horizontal well used for the simulations has a 1000-ft producing section drilled in sandstone with severe bentonite drilling-mud damage along all of it except for a 200-ft long thief zone.

Bullheading 25 gallons of half-strength mud acid removes damage in the first 400 ft of the hole, but fails to make much impact on the section beyond the thief zone (next page, top). The thief zone initially accepts about one-half of the treatment fluid, and with time the upper section becomes a second thief zone. The section beyond the thief zone takes only 20% of the treatment fluid, resulting in poor damage removal.

1. For general reading:
Bullheading acid and diverter in a series of nine alternating stages provides a dramatic improvement (above). The flow rate into the thief zone decreases dramatically once the first diverter stage is pumped, and practically equal flows then go into the lower and upper zones resulting in uniform skin improvement.

By using coiled tubing to inject diverter into the thief zone before pumping acid, virtually uniform penetration can be achieved (left). In the simulation, both upper and lower damaged zones are nearly restored to their natural permeability.

Such effective diversion occurs less readily in carbonates acidized with HCl, where the rapid reaction tends to counter the effectiveness of most diversion techniques. However, field exam-
ples show the benefits of using coiled tubing, rather than simple bullheading of the acid.

In a 1500-ft long horizontal injector in a Middle East limestone reservoir, most of the 4000 B/D injected was entering the first 450 ft of the horizontal trajectory and none was entering beyond 900 ft—see the production log made before acid treatment (right). A treatment was then performed by running coiled tubing to the end of the well and pumping 15% HCl at the rate of 10 gallons per foot as the tubing was withdrawn. When the coiled tubing had been withdrawn to the beginning of the horizontal section, 15 gallons-per-foot additional HCl were bullheaded into the formation. Injection was subsequently 5500 B/D. The post-treatment production log shows most of the increase is entering the first 450 ft of well. But there is some increase between 800 and 900 ft, probably the result of using coiled tubing. There is still no injection beyond 900 ft. Incidentally, no diverters were used in the treatment. Experience in nearby limestone reservoirs using conventional benzoic flake and rock salt diverting agents did not improve coverage significantly.

A second example comes from a horizontal well drilled in fractured dolomite in Shell Canada Ltd’s Midale field, Saskatchewan, Canada. Initially, this pumping well produced 240 BLPD with water cut rising to near 99%.

Logs made with coiled tubing suggested that the well probably intersected the desired fractured dolomite at three separate points—at the heel, midpoint and toe of the horizontal trajectory. Otherwise, it strayed into an overlying tight zone. Production logs, obtained using nitrogen lift with the coiled tubing, showed that the heel zone at low pressure (1200 psi) was not producing, while the toe zone at high pressure (2000 psi) was producing water—probably from the field’s waterdrive scheme. An acid treatment was therefore planned to improve oil production from the heel and minimize treatment of the water zone.

Initially, the entire horizontal section was calculated with foamed gel, resulting in a 90% decrease in injection rate. Then, 10 gallons-per-foot of 15% HCl was injected across two zones near the end of the well while withdrawing the coiled tubing. More diverting foam was then injected. Seven gallons-per-foot of 15% HCl were then injected over a long zone at the heel of the well, again while withdrawing coiled tubing, followed by more diverter and then a repeat injection of acid across the same zone.

The effect of this treatment can be seen by comparing pre- and posttreatment temperature profiles (below). These were obtained by pumping water into the well for a period and then recording temperature along the horizontal trajectory. A temperature decrease with depth indicates acceptance of the cool, injected water; no decrease indicates that no water was accepted and that the zone is unlikely to produce. In this example, considerable improvement can be seen in both the heel and targeted stimulation areas. When the well was put back on a pump, production increased to 300 BLPD, the pumping limit, and oil production increased from 3 to 48 BOPD.
Most recently, Laurent Prouvost and Michael Economides proposed a method that takes into account the transients and can be computed in real time using the Dowell Schlumberger MatTIME job-execution system.\(^{17}\) Their method takes the measured injection flow rate and, using transient theory, computes what the injection bottom-hole pressure would be if skin were fixed and constant—it is generally chosen to be zero. This is continuously compared with the actual bottomhole pressure. As the two pressures converge, so it can be assumed that the well is cleaning up (right). Finally, the difference in pressures is used to calculate skin.

The key to real-time analysis is accurately knowing the bottomhole pressure. This can be estimated from wellhead pressure or, if coiled tubing is used, from surface annulus pressure. The most reliable method, however, is to measure pressure downhole. This can now be achieved using a sensor package fixed to the bottom of the coiled tubing.

Evaluation should not stop once the operation is complete. The proof of the pudding is in the eating, and operators expect to recoup acidizing cost within ten to twenty days. From the ensuing production data, NODAL analysis can reveal the well’s new skin. This can be compared with new predictions obtained by simulating the actual job—that is, using flow rates and pressures measured while pumping the treatment fluids—rather than the planned job. Understanding discrepancies between design and execution is essential for optimizing future jobs in the field.

Just about every area of matrix acidizing, from acid systems to diverters to additives to computer modeling to environmentally friendly fluids has been researched and incorporated into mainstream technique (see “HSE Developments for Acidizing,” far right). The remaining challenge for both operators and the service industry is gaining the same level of sophistication in field practice and real-time monitoring. The tools for improving field operations now appear to be in place. There seems no reason why all matrix acidizing jobs should not be properly designed and executed. The days of the rule-of-the-thumb are over.—HE

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**HSE Developments for Acidizing**

Health, safety and environment issues are being seriously addressed in every corner of exploration and production technology. Laws are tightening and the industry’s obligation to public health and environmental protection cannot relax. Matrix acidizing is no exception.

The technique obviously cannot dispense with dangerous and toxic acids such as HCl and HF, but other fluid additives may be rendered much safer to both the public and the environment. Current examples are inhibitors used to prevent corrosion of tubulars as acid is pumped downhole, and solvents used to clean residual oil deposits and pipe dope from the tubulars.

When acidizing began, it was discovered that arsenic salts could inhibit corrosion. But arsenic is highly toxic and its use was discontinued more than 20 years ago. Less toxic but still harmful inhibitors were substituted. Recently, Dowell Schlumberger introduced the first environmentally friendly inhibitor system, CORBAN 250ECO, that functions up to 250°F [120°C].

CORBAN 250ECO is one of several so-called ECO pumping additives that have reduced toxicity and increased biodegradability. For example, the key inhibiting chemical in CORBAN 250ECO is cinnamaldehyde, a common cinnamon flavoring additive for gum and candy.

Another ECO product made from natural sources is the recently introduced PARAN ECO additive for cleaning oil deposits and pipe dope solvent from tubulars. This is intended to replace aromatic and organic halide solvents that are toxic and that also can damage refinery catalysts if produced with the oil.
Candidate well selection is based on production or water injection history. The design and fluid selection are based on experience—rules of thumb. Job quality control and monitoring often consist of a mechanical pressure gauge and a barrel counter. The current state of technology results in a one-in-three failure rate, with failure defined as the well producing the same or less than before treatment.

It appears that technology advances are motivated by the job cost rather than the potential productivity benefits. What can be done to improve this technology without adding a lot of cost to the treatment?

Candidate Selection and Job Design
We need a generic matrix design program that will diagnose the degree and type of damage, recommend a fluid type, expected treatment rate and pressure, pump schedule and predict the economic impact of the treatment. The program must make do with the few log data that are generally available for economically marginal wells. A key part of the diagnosis is predicting type and degree of damage based on the formation mineralogy, formation fluid composition and injected stimulation fluid chemistry. Physicochemical models exist, but they do not take into account reaction kinetics and how this affects permeability.

Treatment Placement
Techniques for ensuring placement into a particular zone must be advanced. The current diverter technologies work sporadically and many times do more harm than good. Recent work has shown that even when a positive diversion technique such as ball sealers is used, over one third of the perforations become permanently blocked because the balls permanently lodge in the perforation. Chemical diverters are many times misused or do not meet expectations—rock salt is sometimes used by mistake with HF acid producing plugging precipitates, and so-called oil-soluble resins are usually only partially soluble in oil. We need positive, economic, nondamaging diversion techniques whose effectiveness can be documented. Foam and the use of inflatable packers on coiled tubing are viable techniques for positive diversion.

On-site Quality Control and Job Profiling
To improve treatment efficiency, we need more monitoring and controlling of the job on location—a few service companies provide this option for a nominal fee. This should include testing of the fluids to be pumped—to ensure concentration, quality and quantity. To profile job effectiveness, digitized data are required for real-time, on-site data interpretation and postjob analysis. This data should be used to determine the evolution of skin with time, radius of formation treated and the height of the treated interval.

Continuous Mixing of Acid
All matrix treatments are currently batch mixed. If real-time job monitoring becomes widely available, it will give the operator an idea of the most effective volumes of fluid to pump, when to drop diverters, what the diverter efficiency is, and the depth of damage and height of treated interval. To take advantage of this information, the service company must have the capability and be ready to custom blend the required treatment in real time using continuous mixing. Service companies know how to continuous mix, but so far have not provided the technology for matrix treatment.

Commentary: Carl Montgomery

Over half the wells ARCO stimulates each year receive matrix treatments. But this consumes only 17% of the total ARCO stimulation budget. Because of the relatively low cost of a matrix treatment—ARCO’s average is $5,500 in the lower 48 states of the US—there has been very little incentive to improve matrix treatment technology. While there are more than six sophisticated design programs for hydraulic fracturing available for purchase, there is not a single matrix design program for sale.

Carl Montgomery, technical coordinator of well stimulation for ARCO Oil and Gas Company in Plano, Texas, USA.