Special Acids and Additives to Relieve Wellbore Restrictions

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INTRODUCTION

If any type of treatment is to be used effectively and successfully, a knowledge of both the well and reservoir is necessary. The chemical as well as the physical properties of the rock, guide the selection of materials and techniques.

Nearly all sandstone formations contain calcite, dolomite, sand, clay and other minerals. The amounts of each contained in a given sandstone determine the **chemical composition** of that particular rock. Not all sandstones of the same composition, however, respond to acid in the same manner. Not only the amounts of these materials present in a rock, but where they are located and how they occur are of extreme importance.

The **physical structure** of the rock as well as the over-all chemical composition will determine response of the rock to acid. A knowledge of the physical properties of the rock is necessary so that the correct amount of a given chemical and the technique of placement can be selected.

WELL AND RESERVOIR CONSIDERATIONS

Some of the physical properties of both the rock and reservoir are:

(1) Permeability
(2) Porosity
(3) Hardness
(4) Thickness
(5) BHT
(6) BHP
(7) Oil and water saturation
(8) Pfg
(9) Production history

Of all these physical properties of a formation, there is only one that can be changed. This one property is **permeability. Permeability** is the primary objective of all well stimulation treatments. Such treatments are designed to restore or increase natural permeability or establish highly conductive flow paths into the wellbore, so that the productive capacity of the well is increased. This paper will be concerned with chemicals and techniques designed to restore or increase natural permeability near the wellbore.

Knowledge of productive capability of any well is important before as well as after stimulation. If the well is not capable of a profitable rate of production either before or after stimulation, there is no point in treating. If it can be made capable of producing at a desired rate, the question is HOW? Will restoration of natural or original permeability give the desired rate, or will additional permeability or flow paths be needed? The answer to these questions will be determined by the chemical and physical properties of the rock and reservoir.

PROBLEMS AND TECHNIQUES

If it is determined that a well has the capability to produce but it does not do so, then there is an existing problem that must be overcome. For each problem, a given technique of treatment will give the most effective and efficient results.

Since all stimulation treatments are designed to change only one rock property, PERMEABILITY, all existing problems which can be solved or corrected can be divided into two types. They are:

(1) Low natural permeability
(2) Damaged permeability

Low permeability is a natural property of a rock and generally can be overcome only by hydraulic fracturing using a propping agent or by fracture acidizing.

Damaged permeability can be the result of many different things, and the cause will determine the cure as to materials and techniques. Damage is restriction of natural permeability by:

(1) Particle invasion
(2) Mud
(3) Cement
(4) Saturation changes
(5) Deposits

The area where damage or reduced permeability can occur are:

(1) Wellbore
(2) Critical matrix
(3) Reservoir

Matrix Acidizing is concerned primarily with the wellbore and critical matrix. The wellbore is considered as the perforations and face of the formation. The critical matrix is considered as the first three feet of formation out from the wellbore. Permeability damage in this critical zone can greatly reduce production of liquids and gas. Damaged permeability can be determined by a comparison of the productive capability of a well with the actual production. A knowledge of the physical and chemical properties of the reservoir and rock, along with such information as drill stem tests, pressure build-up curves, and production history, will help determine if permeability damage exists.

Figure 1 is a plot of per cent of original flow versus radial extent of damaged zone, and shows the effect of permeability damage in the critical matrix (first three feet). Fifty per cent damage can reduce flow to 75 per cent of original flow. Eighty per cent damage will reduce original flow to 45 per cent.

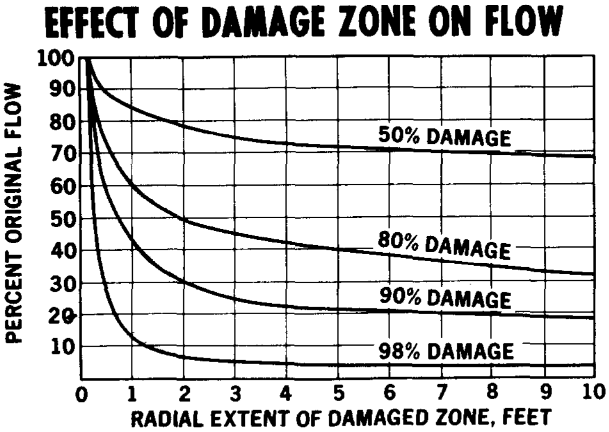

Figure 1

Figure 2 is a plot of per cent of original productivity versus inner radius of damage, and shows the effect of shifting a damage collar out from the wellbore by removing the damage or pushing it out from the wellbore. For example, a damage collar 12-in. thick, located one foot from the wellbore, will reduce flow to 75 per cent of original. If this same 12-in. collar is located three feet from the wellbore, it will reduce productivity to only 90 per cent of original or undamaged flow.

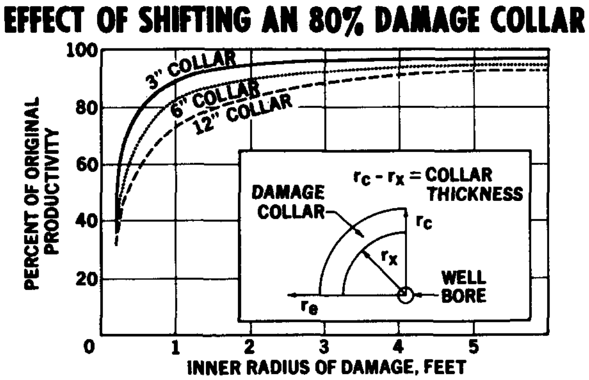

Figure 2

The treating techniques used in restoring damaged permeability are:

(1) Wellbore clean-up
(2) Matrix
(3) Fracturing

Welbore damage is usually the result of scale deposits in perforations and on the face of the formation. Most scales are deposited from produced or injected water. Chemically, they are carbonate or sulfate deposits along with sulfide deposits in wells producing H_2S. The wellbore clean-up technique is a fill and soak operation, in which a chemical is spotted over the section to be treated. The chemical is allowed to soak for a period of time and may be circulated past the section for a time. The chemicals used in this technique are acids and chelating agents. Carbonate scales are soluble in hydrochloric acid, acetic acid, hydrofluoric acid, sulfamic acid. Some sulfate scale is soluble in a chelating agent (EDTA). Other sulfate scale must be removed mechanically. Iron sulfide, a common scale in sour oil and gas wells, is soluble in most acids. An iron stabilizing agent is added to the acid to prevent reprecipitation of the dissolved iron.

While wellbore clean-up will remove damage from the face of the formation, good production increases will more often require removal of damaged materials from within the matrix of the rock itself.

The primary purpose of Matrix Acidizing is to restore permeability. By matrix, we mean the rock itself plus the pore spaces within it. A matrix treatment is one in which the fluid is injected into the rock at less than failure pressure of the rock. Figure 3 illustrates a typical injection-pressure profile. As fluid is injected into a rock, the pressure will increase sharply until at some point (B), the failure pressure of the rock is reached. All treatments performed at pressures less than failure pressure are termed "matrix treatments." Those performed at pressures above failure are termed fracture treatments.

INJECTION - PRESSURE PROFILE

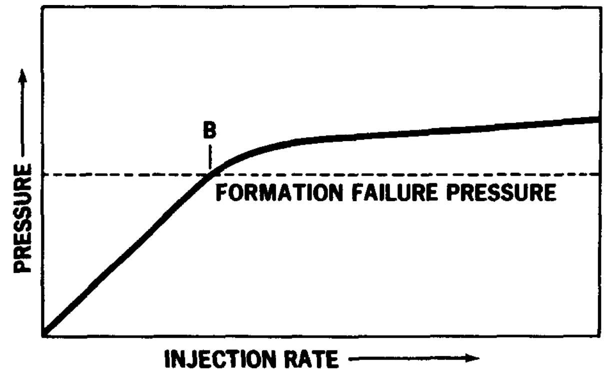

Figure 3

Permeability damage in the critical matrix zone cannot be removed by the fill and soak technique. A matrix injection technique is required. This involves injecting an acid formulation into the matrix pore spaces or into natural or induced fractures.

Induced fractures can be caused from drilling or workover fluids or from cement slurries. Invasion of these fluids cause permeability damage in pores, natural fractures or pressure induced fractures.

The greater the permeability of the rock, the farther the invasion of such fluids. The damage radius in a rock of low permeability that is not fractured may be only a few inches from the wellbore. In this few inches, the permeability reduction may be 90 to 95 per cent, however. In a rock of high permeability, the damage may extend many feet into the rock. Natural or induced fractures can cause extensive invasion and permeability damage by fluids. As mentioned previously, any reduction of permeability in the first three feet surrounding the wellbore has the greatest effect on production.

CHEMICALS AND REACTIONS

There are three types of acid primarily used in welbore clean-up and Matrix Acidizing. They are:

(1) Hydrochloric
(2) Hydrochloric-Hydrofluoric
(3) Acetic

Hydrochloric acid and acetic acid are most used for wellbore clean-up. Hydrochloric-hydrofluoric mixtures are used the most in Matrix Acidizing. Mixtures of these two acids are generally known as Mud Acid.

The following table shows the amounts of material dissolved by one thousand gallons of three different acids used in wellbore acidizing:

Acid	Pounds of Material
15% HCl	1840 — Limestone
15% HAc	1110 — Limestone
2.1% HF	350 — Mud-Clay

Hydrochloric acid will dissolve almost twice as much carbonate material in the form of scale as will acetic acid of the same strength. Hydrochloric acid reacts at a much faster rate than does acetic acid because it is more highly ionized.

Acetic acid will not dissolve as much material as hydrochloric acid, but it can be inhibited for much longer times. Acetic acid is used as a perforating acid because of this.

Mud Acid or HF acid contains approximately two per cent hydrofluoric acid. This hydrofluoric acid will dissolve clay particles found in drilling mud. These clay particles are not soluble in hydrochloric acid or acetic acid.

Special additives are added to the basic acid formulations in order to do a special job. Some of these additives are:

(1) Inhibitors
(2) Surfactants
(3) Complexing agents
(4) Gelling agents
(5) Fluid-loss-control agents
(6) Retarders

All acids used in well stimulation treatments contain inhibitors to protect metal goods against corrosion. **Surfactants** are used to prevent oil-water emulsions and to lower surface tension of fluids. **Complexing agents** are used in acids designed to remove deposits containing iron. These agents prevent the reprecipitation of dissolved iron. **Gelling agents** are used to retard acid by increasing viscosity.

Fluid-loss-control agents reduce acid leakoff from pores and natural fractures. This can result in greater live acid penetration. **Retarders** used in acids slow down the reaction rate between acid and soluble material. This results in longer acid spending times and greater spending distances.

Mud Acid is the most widely used acid in removing damage in the critical matrix zone. The composition of Mud Acid is as follows:

2% HF Acid
13% HCl Acid
Corrosion Inhibitors
Surfactants

When Mud Acid is injected into a sandstone formation, it first reacts with the carbonate material in the form of calcite. Next in the order of reaction is clay materials. After the clay material is quartz. HF acid will react with the calcite ten times faster than with the clay. It will react with the quartz only one-tenth as fast as with the clay. The ingredient that causes the Mud Acid to react with the clay and quartz is the hydrofluoric acid. Calcite is soluble in both hydrochloric acid and hydrofluoric acid.

Secondary reactions of HF acid can produce unwanted product in the formation. The reaction between calcium carbonate and hydrofluoric acid will produce calcium fluoride. Fear of damage due to calcium fluoride precipitation on high-calcite-content rocks has caused considerable concern in the past. **ALL** recent research indicates that calcium fluoride may actually form, but in NO case could a core be plugged with this material.

Calcium fluoride can be prevented from precipitating by the addition of boric acid to the overflush behind a Mud Acid treatment. The use of boric acid in the overflush is recommended when the solubility of the formation in 15 per cent hydrochloric acid is 20 per cent or greater.

It is very easy to form damaging silicofluoride gels through improper use of HF acid. Silicofluorides are jelly-like products resulting from mixing of HF acid with incompatible additives such as sodium or potassium chloride. Formation of these gels can be controlled through use of compatible additives, maintaining a low pH, and a short shut-in time.

MATRIX ACIDIZING

The foregoing discussion has been concerned primarily with what should be known about a well and reservoir in order to use Mud Acid properly, some of the problems it can solve, the techniques, especially Matrix Acidizing, with which it is applied and the chemicals and reactions which make it useful. The remainder of the discussion will deal specifically with hydrofluoric acid stimulation of sandstone reservoirs.

A term which should be introduced at this time is **ACID RESPONSE COEFFICIENT**. The acid response coefficient is a ratio of the acid permeability to the original brine permeability of a core sample. This ARC is determined by flowing two per cent calcium chloride brine through a one-inch diameter core plug. The permeability to brine is determined. Fifteen per cent hydrochloric acid is then passed through the core plug to give a residence time of at least one minute, or until the permeability becomes constant. Mud Acid is then put through the core plug until the permeability either levels off or a two-fold permeability increase is obtained. Permeabilities are calculated from flow rates and pressures which are recorded periodically. The test temperature is usually 75° to 80°F.

The permeability to brine is the original or undamaged permeability. An ARC of one represents restored original permeability. By plotting per cent of original permeability versus acid volume requirements (gal/sq ft), Fig. 4, Mud Acid reaction in a typical sandstone core can be determined.

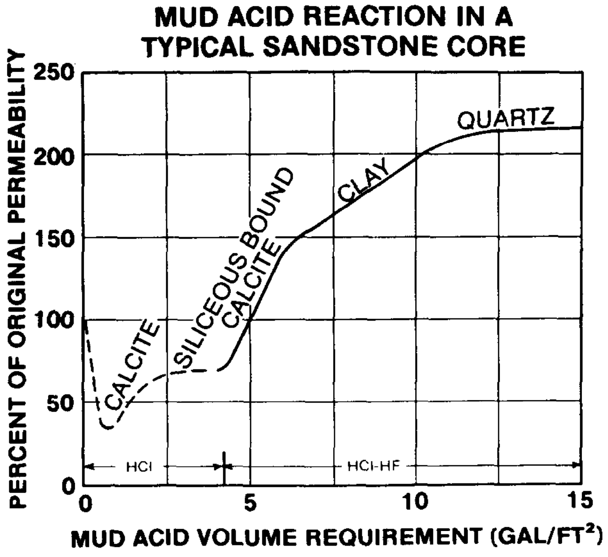

Figure 4

The dashed line section of this curve represents the flow of HCl through the core. The solid line portion of the curve is the Mud Acid reaction. Probably the most important point in sandstone acidizing is shown by this curve. This is the permeability reduction that occurs in most cores after only small volumes of acid have been used.

In the past, many acid treatments may have been stopped in this reduced permeability range because enough acid was not used. As the curve shows, more acid will overcome this initial reduction of permeability. This permeability reduction is probably due to sloughing of clays and fines in the formation as the result of the initial acid reaction. When flow is reversed, these particles act as "check valves" to restrict flow back into the wellbore. If enough acid is used, these materials are dissolved along with other damaging material and an over-all permeability increase is obtained.

This curve also shows the order in which formation material is dissolved by HCl and HF acids. Calcite reacts first with the HCl preflush acid. The HF acid next reacts with the siliceous-bound calcite, then with the clay, and last with the quartz. HF acid will also react readily with the calcite and spend itself. This is why HCl acid is used as a preflush to react with the calcite. This leaves the HF to react with the other material that is soluble only in HF.

Figure 5 shows the response of some actual producing formations to Mud Acid. All of these formations show the initial reduction in permeability described earlier. Three of these formations (the Sparta, Upper Wilcox and Squirrel) have identical Mud Acid solubilities (33 per cent), and very nearly the same HCl solubilities (14 to 18 per cent)—**yet, they do not respond to acid in the same way.**

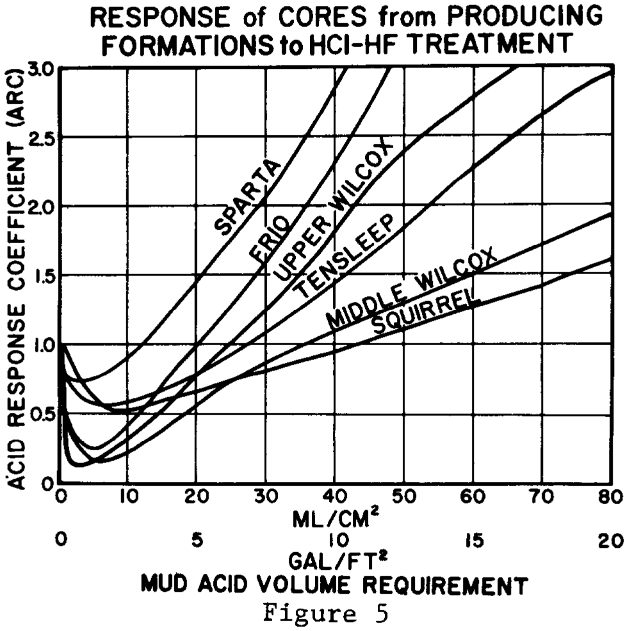

Figure 5

Acid solubility alone has no real meaning. Solubility of a formation sample is usually determined by grinding up the sample to a fine powder. The reaction of acid on this fine powder is then determined. In doing this, the physical structure of the formation material has been changed. Permeability or porosity no longer affect the reaction rate. Only the chemical composition of the rock has not been changed. There is a great difference in flowing acid through a core plug compared to reacting acid with a pulverized sample. Cores with equal solubilities probably have similar chemical composition. They do not respond to acid in the same manner because their physical structure is different.

MATRIX ACIDIZING GUIDE

On acid response curves, the acid volume requirement is shown in "gal./sq ft." The area through which the required volume of acid must pass is the peripheral area at the outer radius of the damaged zone as selected for treatment. This area is calculated by multiplying the circumference in feet, at some distance from the wellbore, by the pay thickness in feet. After the required acid volume is determined from the core plugs, this volume is multiplied by the total area in square feet to give total volume of preflush and Mud Acid. Most treatments are designed to treat a minimum of three feet out from the wellbore. At a three-foot radius, the peripheral area is 18 sq ft per foot of formation treated. For a ten-foot section, the area would be 180 sq ft. If the Mud Acid requirement is 12 gal./sq ft, then the total Mud Acid required would be 180 x 12, or 2160 gallons. Figure 6 shows in graph form the perimeter area versus the damage radius per foot of pay interval.

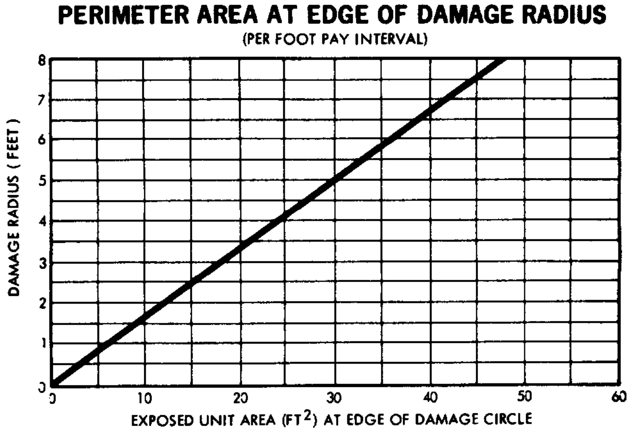

Figure 6

To force the desired volume of Mud Acid to pass through the given cross-sectional area and yet maintain an economical amount of Mud Acid, an overflush fluid must be used to fill the pore space of the rock from the wellbore out-

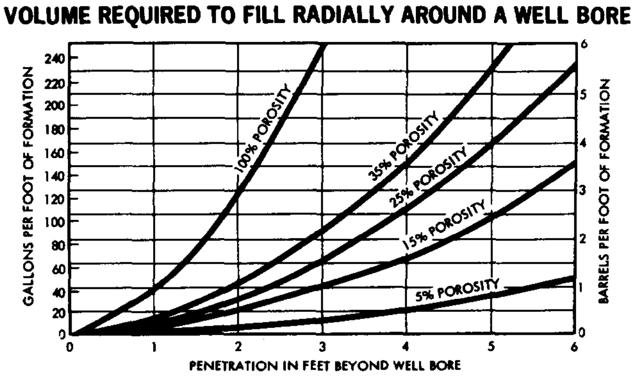

Figure 7

ward to the peripheral area at the edge of the treatment radius. This will displace the Mud Acid out of the rock and push it past the peripheral area so that the total volume of Mud Acid will move through this area.

The overflush volume required is a function of the pore space in the rock (porosity) and the penetration in feet out from the wellbore. Figure 7 illustrates this required volume determination by plotting gallons per foot of pay versus penetration in feet for rocks of varying porosity.

The overflush fluid can be fresh water, clean crude oil, or 5 per cent HC1. Salt water should not be used as overflush. As discussed earlier, sodium chloride can cause formation of silicofluoride gels, resulting in permeability damage.

CONCLUSIONS

Preflush, definite Mud Acid volume, and overflush are needed for an engineered Mud Acid treatment to remove damage in the critical matrix zone. Misuse of Mud Acid through "unengineered" treatments can result in poor results and a waste of money. Based on this informaiton, an ideal treating procedure might be:

(1) Preflush — HC1
(2) Inject HF — HC1 mixture
(3) Overflush — HC1
(4) Short shut-in

If properly planned and applied, taking all factors and conditions into consideration, Matrix Acidizing treatments often can result in satisfactory production increases at reduced cost to the operator.