IMPROVEMENTS IN IN-SITU CROSSLINKED ACID SYSTEMS FOR STIMULATION DIVERSION IN LONG CARBONATE SECTIONS

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ABSTRACT

Polyacrylamides hydrated in hydrochloric acid and crosslinked with iron-based ions have been utilized for a number of years as in-situ divertors in the stimulation of extended-length carbonate zones.

A significant improvement to this process has been developed, field-tested, and placed into general use. Crosslinking the polyacrylamide with a zirconium-based metallic ion has proven to be an alternative with a number of advantages over existing systems. Dependency of the system on iron derivatives for crosslinking is eliminated, the precipitation of ferric or ferrous compounds that can cause sludging or stabilize oil/water emulsions is minimized, and viscosity degradation of the in-situ crosslinked acid is not completely dependent upon the rising pH of the acid as it spends. An external breaker is added to the system as an aid in apparent viscosity reduction.

Case histories are briefly reviewed. Treatment design data, including fluid friction pressure curves and rheologies are presented for use by the practicing engineer. Input parameters suitable for the most common 3-dimensional fracturing and matrix stimulation modeling simulators are included.

INTRODUCTION

Acid-fracturing systems that crosslink upon spending in carbonate lithologies have been available in the industry since the early 1990's[1-4]. Early theoretical claims that in-situ crosslinked systems can be effective in providing some degree of diversion in both matrix and hydraulic fracturing treatments seem to have been substantiated by a number of operators over the years. Historically, these systems have included 3% to 28% hydrochloric acid gelled with a polyacrylamide, with crosslinking initiated as the acid spends to a pH off two. If the development of the crosslink occurs in a low shear rate environment (such as a worm-hole or fracture tip), then it is possible that the resulting apparent viscosity may be high enough that significant shear stress could be required to continue the propagation of the fluid at that particular location. If additional reservoir rock with 500 psi (or less) in-situ stress differential [from one portion of the reservoir to another] were exposed to the fluid, continued pumping of non-crosslinked fluid would then be diverted to a new portion of the fracture, or new fracture volume could be created. Even if the high apparent viscosity of the fluid is not high enough to force a new fracture in a new part of the zone, certainly there is enough apparent viscosity to prevent the severe leak-off and worm-holing that might otherwise occur if this fluid were not present. Observations from numerous treatments both during this study, and prior to it, reveal log-log [Nolte] slopes temporarily approaching 1.0, indicating restricted fracture extension at the fracture extremity[5]. Nierode and Kruck[6] and others’ have shown that effective fluid loss control is paramount to fracture extension in carbonates.

An advantage of this process has been that the incremental friction pressure due to high apparent viscosity originates outside tubulars, and adjacent to the reactive formation. The friction pressure inside tubulars, therefore, remains nearly constant, resulting in a number of unique and advantageous situations:

a) The bottom hole fracturing pressures calculated from the surface treating pressure measurements are more accurate than when a fluid exhibits significant real-time rheological changes during pipe transit (P).
b) A common horizontal wellbore configuration involves placing a pre-perforated non-cemented liner inside an open hole (see Figure 1). The pre-drilled perforation size and spacing is planned such that an even distribution of treatment fluid is promoted. Under these circumstances, a predictable tubular friction of the in-situ system is a basic requirement.
c) Since crosslinking occurs outside the tubulars, the tubular friction pressure gradient is substantially independent of fluid transit time, allowing significant latitude in designing various wellbore configurations and treatment pump rates.

INDUSTRY CONCERNS

Initially, these systems crosslinked a polyacrylamide with iron-based derivatives. As the pH of the spending acid rose above two, crosslinking was initiated and then accelerated. As the pH continued to rise above four, the crosslink would break, and the system rheology would return to approximately the pre-crosslinked state. External breakers were added to the systems in low-temperature and low reactivity situations where the rise to a pH above four was expected to be excessively slow. Occasionally, in moderate to high-temperature applications, buffers were added in an attempt to slow spending in the pH of interest. Research was undertaken to specifically address the industry's concerns with existing in-situ crosslinked acid systems that includes:

1) The use of ferric iron derivatives as crosslinkers and the possibility that harmful and insoluble precipitates or sludges could be formed during or after crosslinking.
2) The inability to utilize even minor concentrations of iron control additives (chelators or reducers) to prevent iron dissolved from the tubulars, tanks, and surface equipment **from** precipitating upon spending.
3) The low pH range (two to four) of the crosslink. It was theorized that a higher pH range could extend the life of the crosslink to a matter of hours (rather than seconds or minutes), and thereby enhance the effectiveness of the diversion and leak-off control that the crosslink enabled.
4) The development of consistent, measurable, and high apparent viscosity. Previous systems were difficult to quantify with respect to crosslink viscosity.
5) Dependence on pH as the sole breaking mechanism. A more positive breaking mechanism that would enhance the breaking effect of pH and was applicable over a wide range of temperatures was preferred.

VELOPMENT OF A NEW IN-SITU CROSSLINKED ACID DIVERTER SYSTEM

The unique ability of a specific zirconium derivative to crosslink in low pH fluid environments and its ability to crosslink polyacrylamide polymers led to the development of the improved in-situ crosslinked acid system. A specific polyacrylamide polymer is dispersed and allowed to hydrate in a hydrochloric acid of concentrations of from 3% to **28%.** The zirconium crosslinker is then dispersed in the acid/polymer solution as it is pumped downhole. As the unspent hydrochloric acid (pH zero) reacts with the soluble carbonate reservoir, the pH rises correspondingly. Crosslinking is initiated as the fluid reaches a pH of **3.75,** reaches a peak crosslink viscosity at a pH of **4.3,** and maintains significant crosslink viscosity through a pH of approximately **5.75.** Further increases in pH break the crosslink, with or without the aid of an external breaking mechanism, although the external breaker enhances the degradation process (see Figure **2).**

SPECIFIC IMPROVEMENTS

The new In-Situ Crosslink Acid Diverter was improved as follows:

1) The complete elimination of iron derivatives as crosslinkers.
2) Moderate iron control (5,000 ppm **3:1** ferrous:ferric) is possible with the new system. Shaughnessy and Kunze[8] and others[9] have documented the impact of allowing ferric and ferrous iron held in solution to precipitate as acid spends. Although it is probable that the precipitation of Fe(II) carbonate (siderite, $FeCO_3$) may not pose a significant hazard to production because of its tendency to form a crystalline scale that adheres to porkwalls at high **(< 7.5)** pH, it is possible that Fe(III) in solution could precipitate as iron hydroxide [$Fe(OH)_3$ ——— an insoluble, gel-like material that can mobilize toward pore throats and inhibit production. Smith, Crowe, add Nolan[9] reported that iron hydroxide precipitation is initiated at a pH of **2.2,** and is quantifiable at a pH of **3.2.** The new systems allows the reduction of reasonable quantities of iron (III) that might be found in surface frac tanks and in tubulars to iron (II), thereby lowering the risk of iron hydroxide precipitation in the formation. If the reservoir fluid in place is primarily oil, then these same iron control additives may be employed in conjunction with appropriate surface-active agents to effectively reduce the risk of sludging.
3) The crosslink pH range extends from **3.75** to **5.75.** Acid spending rate is a logarithmic function dependent primarily on the reactivity of the rock, the temperature, and the hydrogen ion concentration at any given point in time. The improved system crosslinks at a higher pH range, thereby extending the life of the crosslink and ensuring that the treatment may be completed prior to crosslink break. (Note: A pH of **4** is 10 times more basic than a pH of 3; a pH of **5** is 100 times more basic; and a pH of 6 is 1000 times more basic).
4) Apparent viscosities of the crosslinked system are higher than conventional systems utilizing iron derivatives for crosslinking (see Figure 3).
5) A special synergy with CO_2 was observed. CO_2 in solution tended to stabilize the crosslink slightly longer than systems without CO_2. When an external breaker was employed, rheological degradation was enhanced (see Figures **4** and 5), but such degradation eventually took place with or without the external breaker. It was hypothesized that when CO_2 was present, the overall breaking mechanism was a function of a) thermal degradation, b) thermal thinning, c) production or reaction of the carbonic acid [and subsequent rise in **pH],** and, d) the action of the external breaker.

FLUID AND ROCK INTERACTION PROPERTIES

An initial attempt was made to mathematically characterize the reaction rate parameters associated with the new fluid and a reactive rock with known properties. The parameters Reaction Rate Coefficient (K), Reaction Order (n), Flux (u), Activation Energy (E_a), Diffusivity (D), and Activation Energy as it relates to Diffusion (E_D) may be measured or calculated for a reactive fluid and rock combination[14-16] (see Figure 6). It is highly questionable, however, whether such observations and calculations have any tangible meaning, for the following reasons:

1) The differential equations that describe heat transfer and acid reaction in porous flow channels have been solved and described by Terrill[10] and Nierode and Williams". Unfortunately, they assume that the acid reaction rate at the surface is large compared with the flux of acid to the surface, and they assume that fluid loss is constant along the first 70 to 80 percent of fracture length, which could be realistic for a system that does not become highly non-Newtonian upon spending. These assumptions may not be valid for a fluid that may be crosslinked at the fracture face, or one that exhibits a highly variable [concentration-dependent] fluid loss rate.
2) Laboratory-generated values for the area of a core sample are generally very subjective, and depend upon visual inspections of roughness and relief (the difference in height between high and low points of the surface before and after etching)[12] Not only are these subjective measurements dependent upon the individual observer, but they can vary widely according to particle size, the presence/absence of vugs, and the presence or absence of multiple minerals [of variable reactivity] other than the dominant mineral. The value for the area of the core face is used to calculate the flux (u), which is then used with other parameters to calculate the Surface Acid Concentration (C_s), which is subsequently used to calculate the Reaction Order (n) and the Reaction Rate Coefficient (K).
3) Actual pumping of various in-situ crosslinked fluids above 150 degrees Fahrenheit through the years has consistently revealed surface pressure increases that occur almost instantaneously as the system arrives on the reactive zone. If we assume that this pressure increase is due to crosslinking of the system and subsequent diversion or fluid loss control, then we must also assume that several more variables (and/or processes) must be taken into account in deriving the equations that describe acid reaction in flow through a porous channel. To the author's knowledge, this special case of the derivation has not yet been seriously attempted by anyone in the industry.

There are a number of software packages available that attempt to utilize the above-mentioned characterization parameters for various combinations of acid systems, concentrations, and lithology/mineral types. Table 1 presents parameters associated with a conventional gelled acid/hard-limestone combination, and is reflective of the approach that was used when it was necessary to simulate the acid reaction response with existing models. It was felt that this process would result in the modeling of a conservative geometry and reaction profile, and would provide some degree of consistency when comparing multiple options with each other.

CASE HISTORIES. PRESSURE PLOTS, AND APPLICATIONS

The basis for this paper was a specific series of 24 treatments performed in the Permian Basin of West Texas and Southeastern New Mexico. These are summarized in Table 2. The majority of these treatments were associated with horizontal Devonian completions, but treatments were also performed in Montoya, Wolfcamp, and Abo reservoirs. When production data is not shown, it is because information had not yet been provided to the appropriate state agency at the time of publication.

Figures 8 and 9 are typical pressure/rate plots from these treatments. The crosslinker rates and stage volumes have also been plotted so that the point the in-situ crosslinking becomes active can easily be determined, and can be compared with the point at which the in-situ crosslinked acid arrives on zone. In nearly every case, short-term pressure increases of 100 – 500 psi were noted at or just slightly after the system arrived on zone, indicating that reaction is very rapid, and implying that diversion, if it is taking place, is also initiating rapidly, During the pilot program, as incremental operational and system improvements were made, the overall net pressure increases from the beginning of the treatments to the end increased. There did not appear to be a relationship between production and overall net pressure increase for a given treatment. Because previous authors have indicated that there might exist an optimum ratio between the volume of in-situ crosslinked acid and the slick acid that follows each stage[13], it was decided to limit extreme volumetric variation from these proven practices.

CONCLUSIONS

Significant improvements to conventional in-situ crosslinked acid diverting systems have been implemented and widely accepted. Dependency of the system on iron derivatives for crosslinking has been eliminated, the precipitation of ferric or ferrous compounds that can cause sludging or stabilize oil/water emulsions is minimized, and fluid apparent viscosity development has been improved. Additionally, crosslinking at a higher pH than earlier systems allows higher viscosities to remain in place longer. A special synergy with CO, has been documented that can help stabilize the crosslink for up to several hours.

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Table 1
Typical 3-D Modeling Inputs

Typical Reaction Parameters for Permian Samples

Parameter Name	100% Limestone	100% Dolomite
Reaction Rate Coefficient	6.6 X 1[illegible]	8.0 X 10^6
Reaction Order	0.37	0.40
Activation Energy	4.7	4.0
Diffusivity	2 X 10^{-4}	4 X 10^{-5}

Rheologies, 15% HCl Base System, 15 gpt polymer

Temperature	n-prime	K-prime
70	0.732	0.003543
80	0.721	0.003608
1no	0.696	0.003783
120	0.684	0.003863
140	0.670	0.003988
160	0.645	0.004178
180	0.640	0.004185

Table 2
Production Results from Each of the Treatments in the Study

COUNTY	FORMATION	FIELD	TOTAL ACID VOL	REMARKS
WARD	MONTOYA	BLOCK 16	180265	No Public IP 01/07/02; 180 Day Cums: Gas - 558,508 MCF; Liq - 1286 BBL; Wtr - 4524 BBL
MIDLAND	DEVONIAN	PEGASUS	180000	Public IP 1.432 MMSCFD, 43 BOPD; No public monthly production 01/07/02
MIDLAND	DEVONIAN	SWEETIE PECK	180000	No Public IP 01/07/02; No public monthly production 01/07/02
UPTON	DEVONIAN	BENEDUM	180000	Public IP .227 MMSCFD, 22 BOPD; 150 Day Cums: Gas - 18,389 MCF; Liq - 1,750 BBL; Wtr - 0 BBL
WARD	MONTOYA	BLOCK 16	79800	No Public IP 01/07/02; 90 Day Cums: Gas - 129,331 MCF; Liq - 0 BBL; Wtr - 258 BBL
MIDLAND	DEVONIAN	PEGASUS	165000	Public IP 0.885 MMSCFD, 20.3 BOPD; No public monthly production 01/07/02
EDDY	ABO	ARTESIA	50000	Public IP .020 MMSCFD, 31 BOPD; 90 Day Cums: Gas - 1200 MCF; Liq - 388 BBL; Wtr - 1163 BBL
WARD	MONTOYA	BLOCK 16	210000	No Public IP 01/07/02; 90 Day Cums: Gas - 586,838 MCF; Liq - 0 BBL; Wtr - 0 BBL
LEA	WOLFCAMP	JOHNSON RANCH	40000	No Public IP 01/07/02; 60 Day Cums: Gas - 1201 MCF; Liq - 317 BBL; Wtr - 57 BBL
MIDLAND	DEVONIAN	WAR - SAN	225000	Public IP 1.525 MMSCFD. 315 BOPD; No public monthly production 01/07/02
LEA	WOLFCAMP	EIDSON RANCH	15000	Public IP .039 MMSCFD, 36 BOPD; 90 Day Cum: Gas - 483 MCF; Liq - 543 BBL; Wtr - 811 BBL
UPTON	DEVONIAN	BLOXOM	246000	Public IP 6.388 MMSCFD. 318 BOPD, 136 BWPD; 60 Day Cums: Gas - 343,412 MCF; Liq - 17,009 BBL; Wtr - 7,311 BBL
TERREU	DEVONIAN	SE SHEFFIELD	190000	Public IP 6.239 MMSCFD, 45 BOPD; No public monthly production 01/07/02
TERRELL	DEVONIAN	SHEFFIELD	141000	Public IP 1.791 MMSCFD. 8.35 BOPD; No public monthly production 01/07/02
UPTON	DEVONIAN	WILSHIRE	130495	Public 1st prod test 2.1 MMSCFD, don't know if pre or post-frac; No public monthly production 01/07/02
WARD	DEVONIAN	BENEDUM	186500	No IP or public production available 01/07/02
REEVES	MONTOYA	WAHA	131000	No IP or public production available 01/07/02
MIDLAND	DEVONIAN	PEGASUS	52164	No IP or public production available 01/07/02
MIDLAND	DEVONIAN	PEGASUS	111846	No IP or public production available 01/07/02
UPTON	DEVONIAN	BLOXOM	106251	No IP or public production available 01/07/02
COCHRAN		LEVELLAND	133000	No IP or public production available 01/07/02
LEA	WOLFCAMP	JOHNSON RANCH	60000	Public IP 2.52 MMSCFD, 420 BOPD; No public production 01/07/02
UPTON	DEVONIAN	WILSHIRE	78372	Verbal report from operator 3.1 MMSCFD 01/09/02
TERRELL	DEVONIAN	BROWN-BASSETT	138386	Verbal report from operator on 01/09/02: 7.1 MMCFPD; No public production 01/07/02

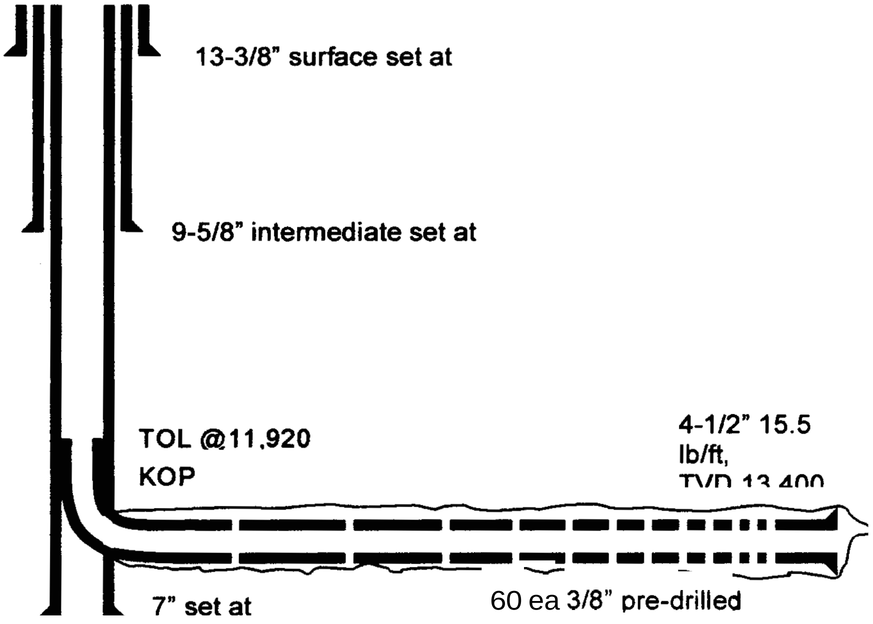

Figure 1 - Typical "Sprinkler System" Wellbore Geometry

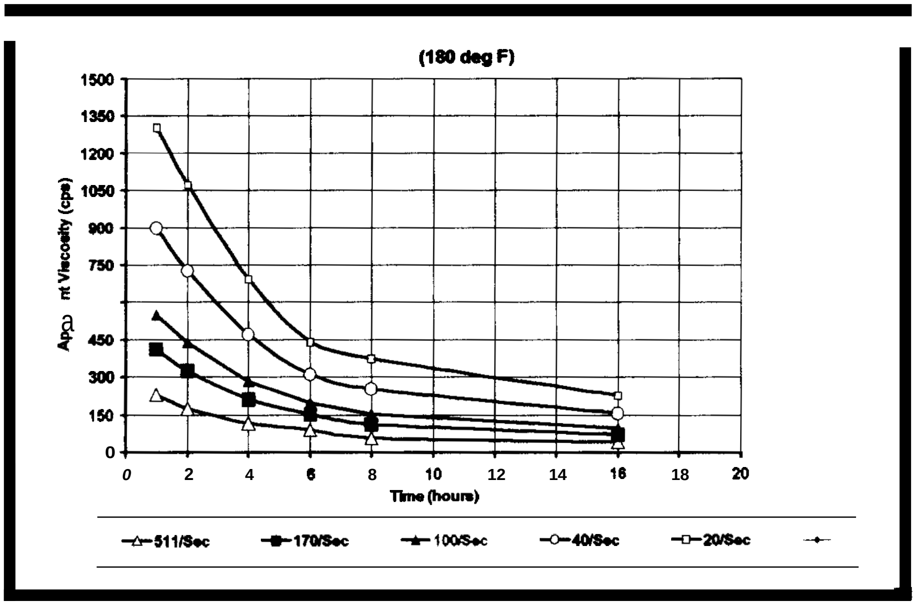

Figure 2 - Impact of Time on System Break

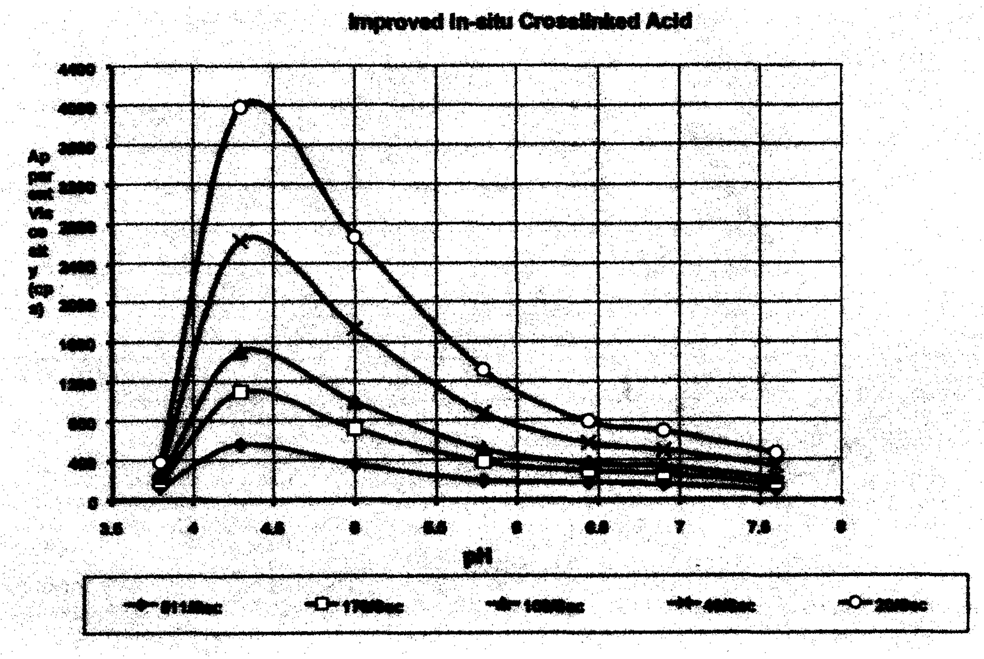

Figure 3 - Crosslinking Range of the New Improved System

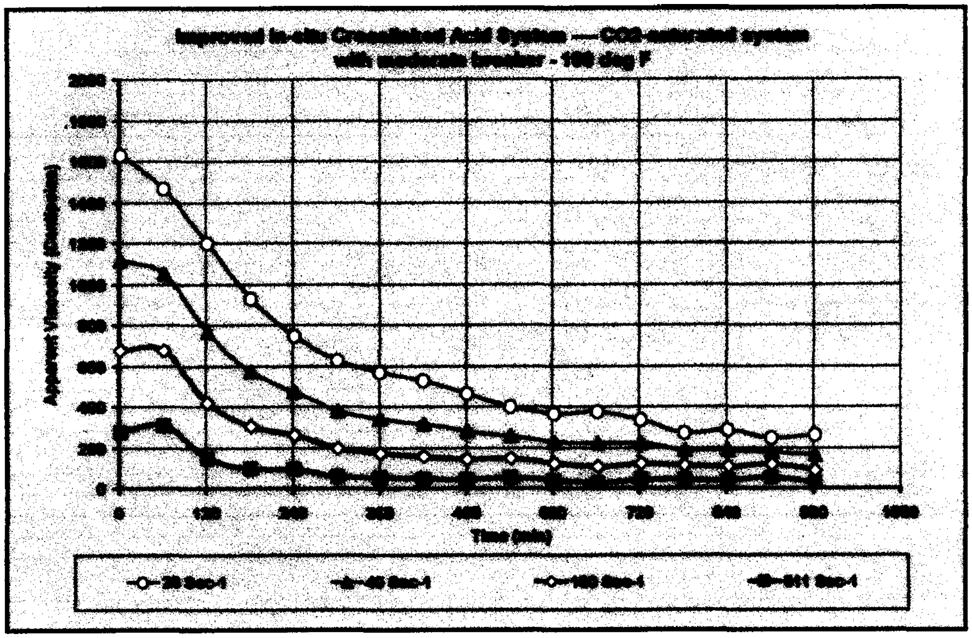

Figure 4 - Synergy with CO,. With this particular system, two to four hours of acceptable crosslink is possible. .

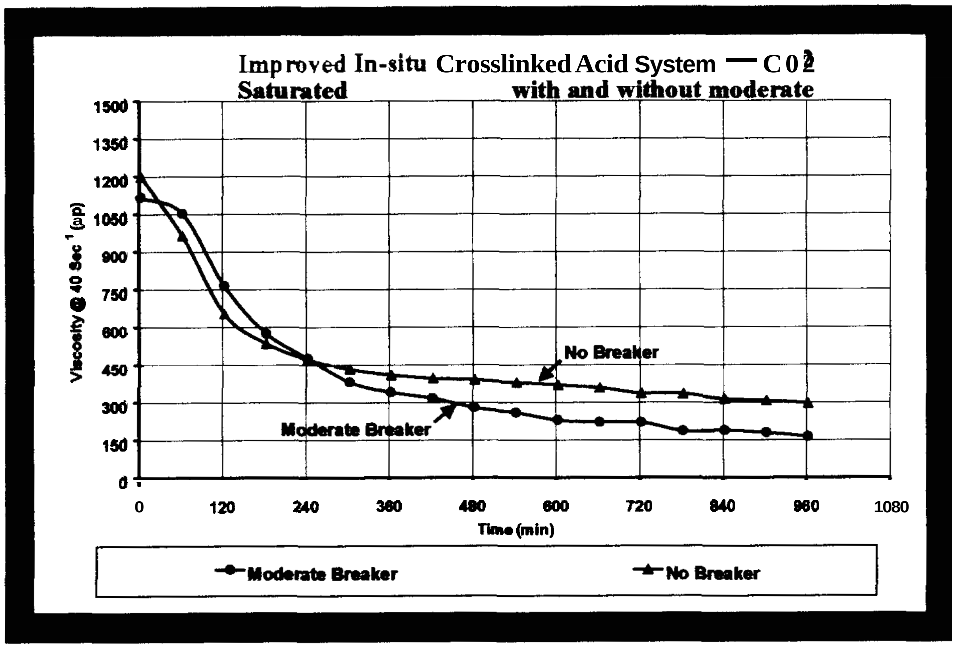

Figure 5 - Impact of a Moderate Quantity of External Breaker on a CO_2-Saturated System

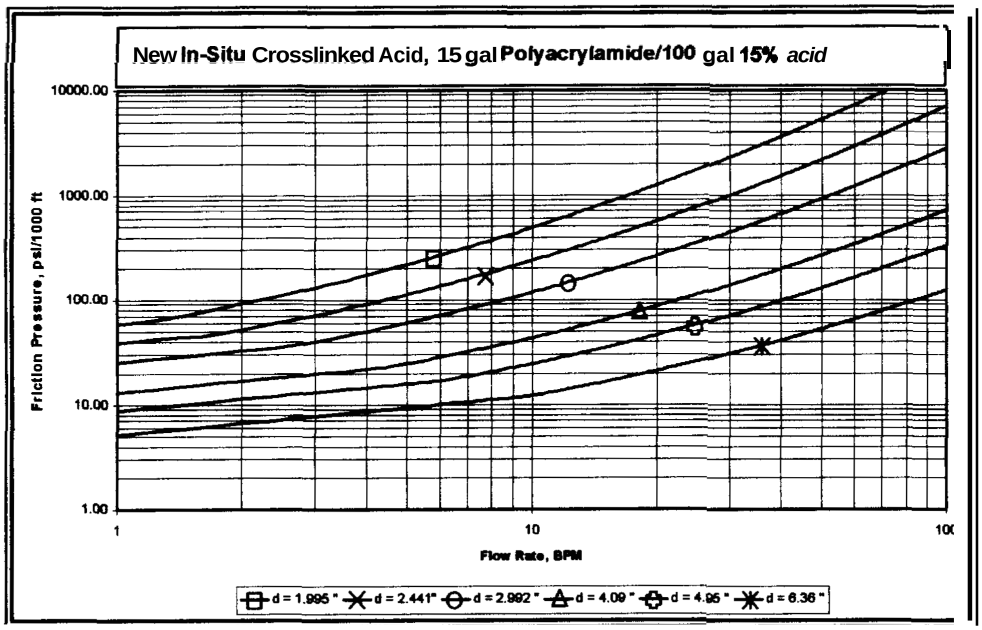

Figure 6 - Friction Pressures Associated with the System (no CO,)

$\dot{V}''_{loss} = 2v_{yl}\lambda_l + 2V_{yp}(1-\lambda_l)\lambda_{fl} + \dot{V}''_{wormholes} + 2V''\lambda_l - 2\dot{V}''_R\lambda_l$ where

$2v_{yl}\lambda_l$ = leakoff in the carbonate
$2V_{yp}(I - \lambda_l)\lambda_{fl}$ = leakoff in the non-carbonate
$\dot{V}''$ = leakoff
$2V''\lambda_l$ = change in volume due to diffusion
$2\dot{V}''_R\lambda_l$ = change in volume due to the reaction products

$V = K(C_s)^n$ where

V = **flux** or reaction rate **(gmole/cm^{2}sec)**
K = reaction rate (units depend on n)
C_s = acid concentration at the fracture surface
n = reaction order (dimensionless)

$K'_T = K'_{To}\,exp\left[\frac{E_a}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right]$ where

K'_T = adjusted reaction rate coefficient
K_{To} = reaction rate at reference temperature T_o
E_a = activation energy for reaction rate, cal/gm - mole
R = **gas** law constant, 1.987 cal/gm - mole

$N_{sh} = \frac{K_g W}{D}$ **where**

K_g = mass transfer coefficient
W = fracture width
N_{sh} = Sherwood number
$\boldsymbol{D}$ = diffusivity

and $D_T = D_{To}\,exp\left[\frac{E_D}{R}\left(\frac{1}{T_o} - \frac{1}{7}\right)\right]$, where

D_T = diffusivity at temperature T
D_{To} = Diffusivity at reference temperature T_o
E_D = activation energy for diffusion, cal/gm - mole
R = **gas** law constant, 1.987 cal/gm - mole

Figure 7 - Simplified Equations Governing Reaction Rate with Various Rock/Acid Combinations

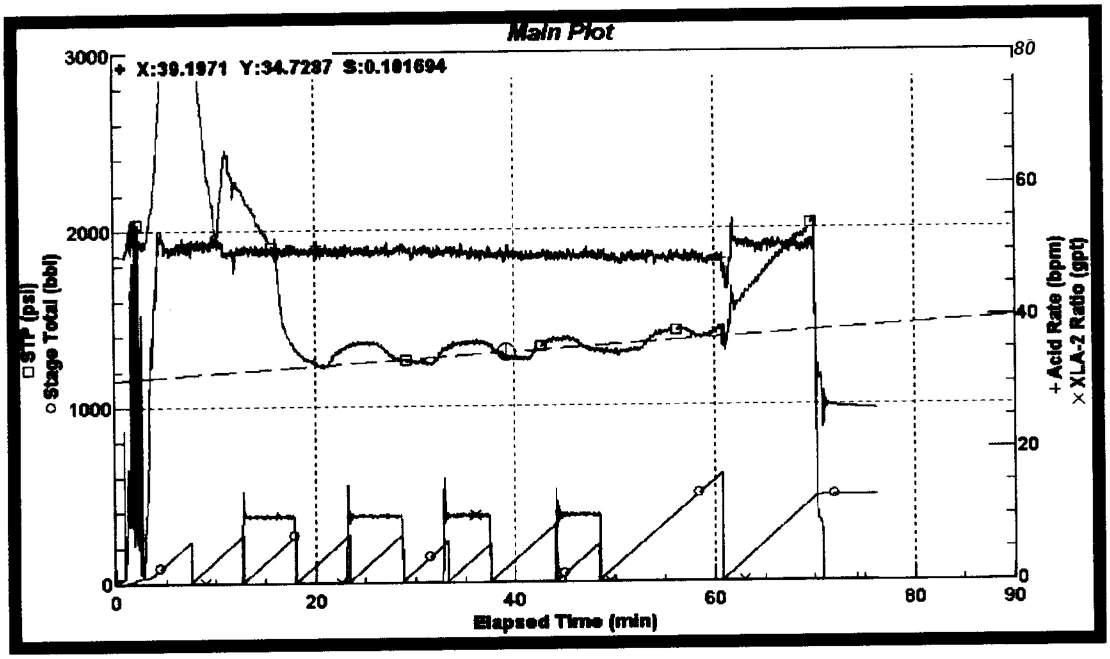

Figure 8 - Example Pressure-Rate Chart. The "XLA-2" ratio indicates when crosslinker was pumped at the surface. Pressure rises just as it arrives on the formation. This well produced significant quantities of oil after the treatment.

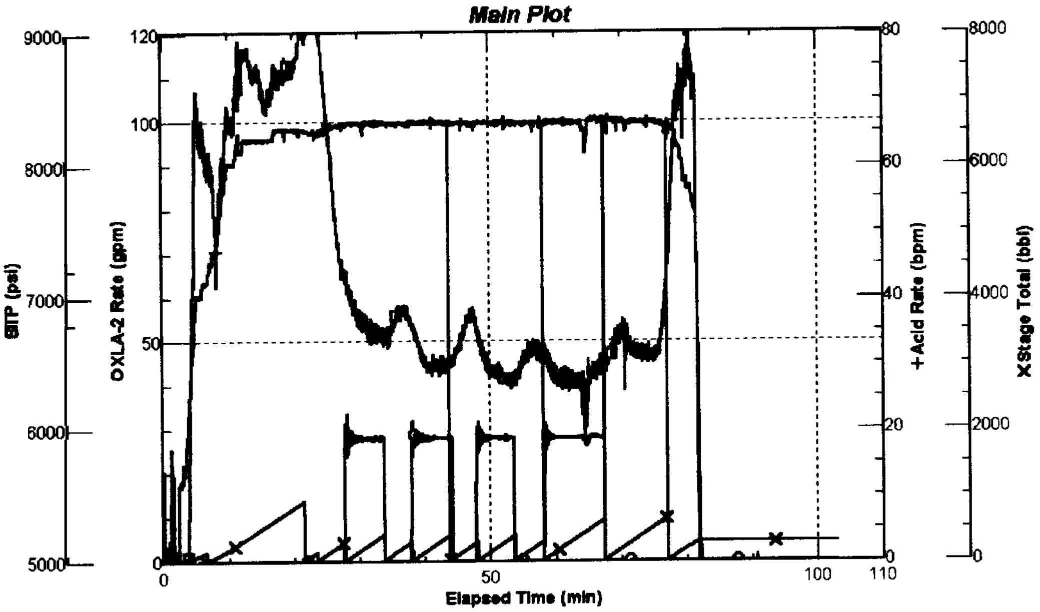

Figure 9 - Another Example Pressure-Rate Chart. Although net pressures decreased during portions of this treatment, the well produced significant quantities of gas and condensate.

Figure 10 - Improved In-Situ Divertor at a pH of about 4.3