HIGH TEMPERATURE, CROSSLINKED HIGH STRENGTH ACID SYSTEM

Michael A. Smith, Jeff Dawson, Dan Scoggins
Dresser Titan, Dresser Industries, Inc.

ABSTRACT

Fracture acidizing systems previously available are acid and temperature sensitive. This paper will discuss a new crosslinked acid system that is compatible with up to 28% HCl and that has been successfully pumped at bottom hole temperatures to 250°F.

Fluid rheology, friction pressure, fluid loss, additive compatibilities and acid reaction rates supporting the use of this system at 50 and 60 lbs./gal. polymer loadings are presented.

Computer designs for acid fracturing and reservoir simulation are included in the paper to show the effects of the stable crosslinked acid compared to other available systems.

This system has been used both with and without proppant. The acid concentrations have ranged from 3% to 28% HCl and where applicable sand concentrations from 2 to 6 lbs. per gal. have been successfully placed. Field data is presented for both producing and water injection wells.

DISCUSSION

Since gelled and crosslinked acids have been available for a sufficient length of time to evaluate each system, it was considered important to determine the limitations of each system and attempt to improve on them. Based on publications and standards set by the oil industry, specific requirements can be developed for an ideal crosslinked acid system.[1,2,3] These requirements are:

1. It must have the characteristics of a good fracturing fluid such as low friction pressure, low fluid loss, be residue free when broken, be temperature stable, and possess excellent proppant transport properties.
2. We must be able to place the material in the formation prior to significant spending. It should react as it moves back toward the wellbore while maintaining enough viscosity to carry any insolubles out of the created fracture.

Tests were run to 100°F in 15% HCl to determine the stability of guar gum, hydroxypropyl guar, hydroxyethyl cellulose, carboxymethylhydroxyethyl cellulose, xantham gum, and a proprietary acid stable polymer. The xantham gum and the proprietary polymer were the only materials that exhibited stability. However, at 150°F in 15% HCl, a 60 lb./1000 gal. concentration of xantham gum exhibited a 73% reduction in viscosity within 45 min. (Fig 1). Fig. 2 reveals that a crosslinked formulation utilizing the proprietary polymer remains viscous for more than twice as long. Gels with 50 lbs./1000 gal. of crosslinked polymer exhibited an increase in viscosity as temperature was increased from 110°F to 160°F before beginning a slight decline (Fig. 3). During these tests the gels were heated for 1 hr. with a final reading of 50 cps at 220°F. Cellulose systems are limited due to hydrolysis of the base gel at moderate temperatures moderate acid strengths, and limited time, (110°F, 7½% HCl, 1 hr.). Guar base systems and substituted HPG all produced similar test results. Cellulose or Guar systems cannot successfully be used even in low temperature applications unless they are continuously mixed as pumping takes place to prevent partial or complete loss of viscosity. The degrading time will limit pumping time at varying bottomhole conditions.

Based on the above results, additional testing was performed on the proprietary polymer. It was necessary to determine the time that the polymer remains stable in acid. It was found that the new polymer maintains stability in 28% HCl for over 72 hrs., thus making it possible to gel the acid the day before pumping. It was also determined that the polymer's stability would allow for heating the fluids if necessary to protect against tubing contractions.

The viscosity of this system is controlled by a proprietary complexing agent which is added to the system while pumping. Complexed acids currently available require extended time (1.5 to 2 min. minimum) for crosslinking.[2] This new system uses a two step crosslinking reaction. The initial crosslinking yields a near perfect sand transport system (Table 1).[4] This occurs within 30 sec. A second step occurs with elevating temperature. Previous crosslinked acid systems exhibit a 20 to 40% reduction in tubular friction pressure,[2] whereas this new crosslinked acid has yielded 65% reduction on actual treatments. Friction reduction values for different rates are shown in Fig. 4, and are compared to those of a water based crosslinked system.

Previous crosslinked acid systems have had the potential for formation damage from unbroken gel and insoluble fines.[1] This unique crosslinked acid gel does not precipitate as do many other synthetic polymers.[4] Once the fluid is in the fracture and the acid is spent, the polymer inverts from mildly cationic to anionic thus becoming a brine soluble polymer which will not precipitate even when completely neutralized in the presence of calcium ions.

A new patented breaker system is used to produce a timed controlled break-out. This material reduces the system's viscosity to approximately 10 cps. This is sufficient to return insolubles without sacrificing cleanup time. Because the break can be controlled, the acid can be put in place and broken with a minimum reduction in acid strength.

Meeting the requirement of placement of the material in the formation before it reacts can be extremely important. This is not only the case in highly soluble formations but also in sensitive sandstone formations, where the low pH of acid gel systems can help to minimize clay damage. This new crosslinked acid's inherent ability to inhibit clay swelling and its proppant transport capabilities provide distinct advantages over fracturing treatment designs currently used in some sandstone formations such as the Canyon and Morrow Sand formations of West Texas and New Mexico. The Canyon and Morrow Sands historically yield better to initial production and slower production declines when treatments utilizing high sand concentrations are performed. This new crosslinked acid system will not only carry high concentrations of proppant but maintain a low pH during flowback.

Reaction rate tests were performed on available cores under static and dynamic conditions (Tables 2, 3 and Fig. 5). Dynamic acid reaction rates were also run on 100% limestone to illustrate a comparative example under extreme conditions. This data reveals that the newly developed system will in fact allow placement of high strength acid into the formation before significant reacting can take place. With the controlled breakout, cleanup can be started almost immediately allowing reactive acid to etch the fracture face as the fluids returns.

The lower pH maintained by this crosslinked system will not allow iron precipitates to drop-out. Actual flowback samples showed a pH of less than 1 and samples taken from two field cases had maintained a pH of 3 to 3.2 after 48 hrs. Additional iron controlling agent can be added to this system if needed.

In listing some of the properties of this new acid system it is evident that this system meets the requirements of a good fracturing fluid.

- o Friction is 60% less than unaltered acid.
- o $C_{III} = 8.82 \times 10^{-4}$ FT/ $\sqrt{MIN}$
- o Spurt loss = 0
- o A breaker that provides a totally residue free and controlled break.
- o Viscosity at 150° after ½ hr. = 200 cp
- o Viscosity at 150° after 1½ hr. = 65 cp
- o Near perfect sand transport.
- o The reaction rate is near zero while complexed and after breaking remains significantly slower than unaltered acid.

APPLICATION

This newly developed crosslinked acid system can be used in various formation treatments where other acid treatments have been used in the past. It can be utilized:

1. As a replacement for HCl in virtually any acid fracturing treatment.
2. As a replacement for foam or emulsified acids where job costs or surface treating pressures are excessive.
3. To reduce or eliminate the pad portion of a pad-acid stimulation treatment.
4. As a replacement for chemically retarded acids where superior retardation and leak-off control are required.
5. As a proppant carrying fracturing fluid for water sensitive formations.

COMPUTER DESIGNS

Results from both acid fracturing programs and a reservoir simulator case study are presented to determine the effectiveness of crosslinked acid and economics based on return on investment. Table 4 represents the etched length at the point where the acid mixtures are 90% spent. Rock properties in the first five examples are based on specific cases. The last three examples were case studies using 100% limestone.[4] These cases are used to illustrate the most reactive conditions possible.

The formation data in Table 5 describes a reservoir simulator case study well and the economics leading to retreatment with crosslinked acid. Fig. 6 graphically shows gas produced as a percentage of gas in place as a function of time. This particular well was produced for 8 yrs. prior to consideration of stimulation. If after 8 yrs. the well was stimulated by any of these three acid systems, unaltered acid, foamed acid or the new crosslinked acid, gas production would increase. After 2 yrs. the unaltered acid would have produced an additional 10% of gas in place, the foamed acid would have produced an additional 15% of gas in place, and the crosslinked acid system would have produced an additional 20% of gas in place. This example shows that even with equal volumes of acid and equal dissolving power the new crosslined acid provided improved stimulation results. To state these results economically, in Table 5, the left-hand figures represent job cost plus 50% related workover expenses. The right-hand figures represent revenue from gas recovered over the non-stimulated case, less job cost, at a gas price of $2.65 per 1000 SCF and a 65% working interest. This data reveals that the new cross-linked acid system is more cost effective.

CASE HISTORIES

Case histories of wells where the crosslinked acid treatments were used are presented in Table 7. Normal considerations as to formation rock properties and reservoir conditions were used to determine the candidates for these treatments. Out of 13 wells pumped to date, 11 have been in the West Texas Area. Available results for 30 days and/or 60 days are reported.

CONCLUSIONS

This paper has presented technical data and well case histories for a new proprietary acid fracturing system. The advantages of this system comes from possessing a combination of properties that are characteristics of an efficient fracturing fluid with those required to slow down and control the reaction rate of an acid mixture on soluble formation rock. These aforementioned properties include:

1. Viscosity stability in acid strengths up to 28% HCl and temperatures to 220°F.
2. Polymer stability in acid, at surface conditions, for up to 72 hrs.
3. Friction pressure properties that allow this crosslinked acid system to generate friction pressures that will be, in most cases, less than that generated by a crosslinked water based system.
4. Fluid loss control that equals or exceeds that achieved by crosslinked water based fluids. This helps to insure deep penetration of live acid.
5. Proppant transport characteristics that approach those of a perfect support fluid.
6. An extremely retarded reaction rate that will, in many cases, allow the crosslinked acid to be placed into the formation with little or no decrease in acid strength.
7. A controlled breakout that effectively allows the acid to spend as the fluid is moving back toward the wellbore during cleanup.
8. A residue free breakout that helps to insure minimal formation damage that could otherwise result from the stimulation fluids being used.

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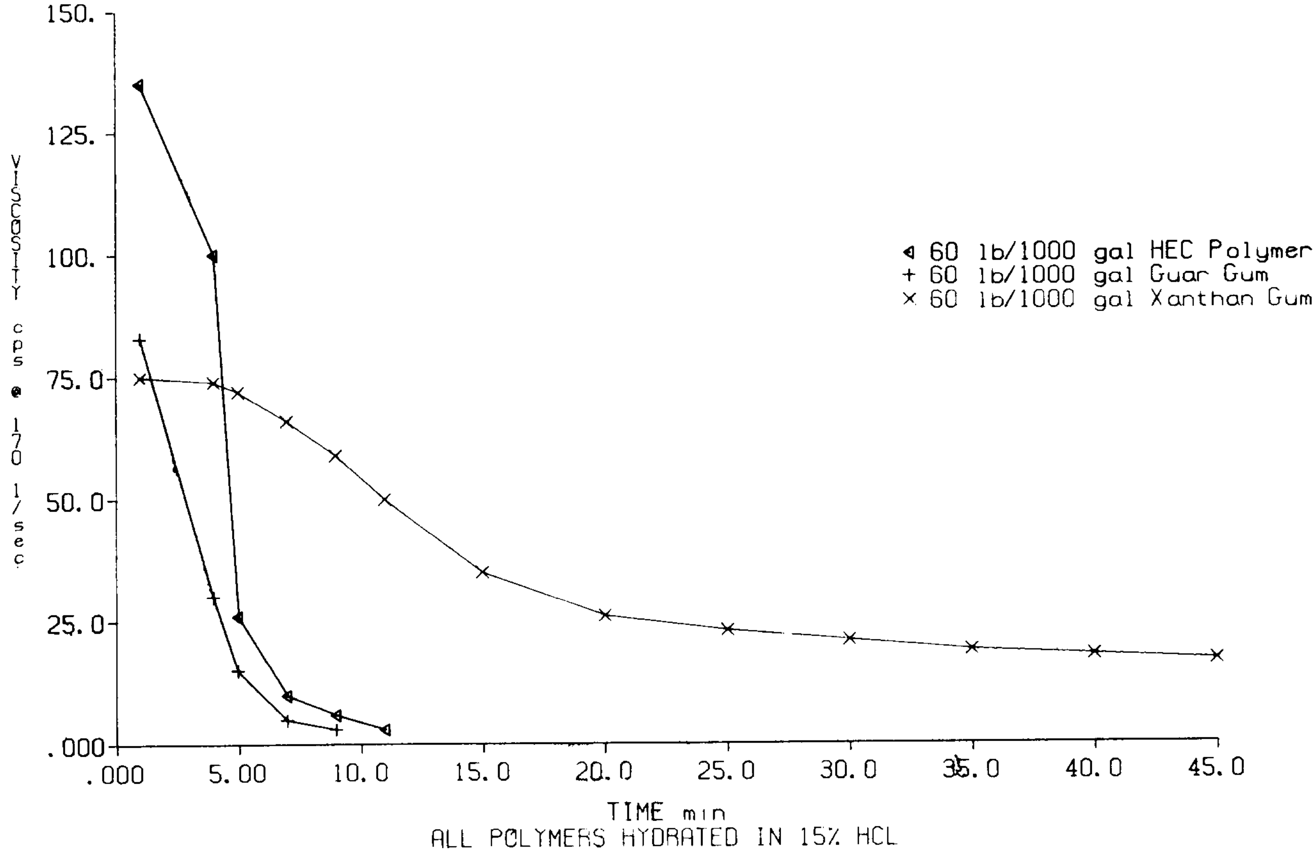

FIGURE 1 — GEL VISCOSITY VS. TIME @ 150 F

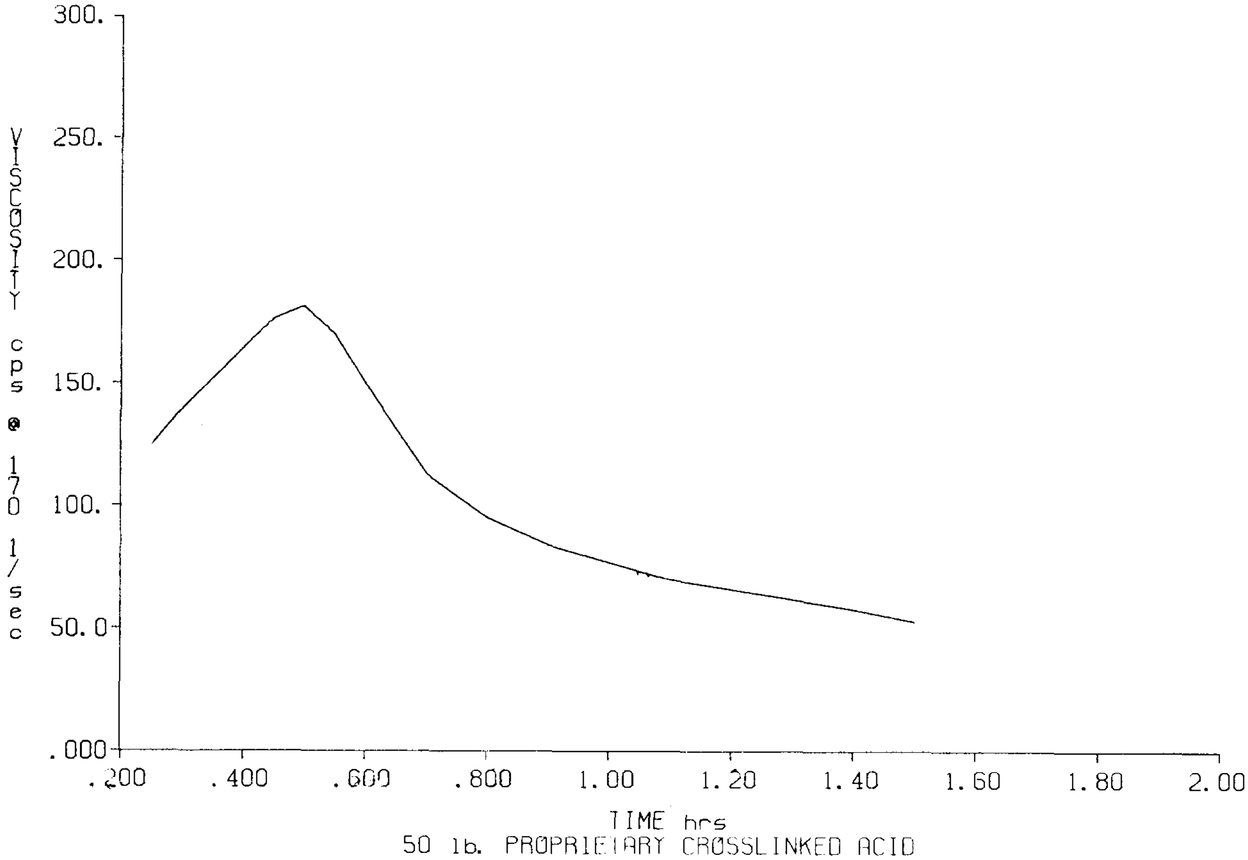

FIGURE 2 — VISCOSITY VS. TIME AT 150 F

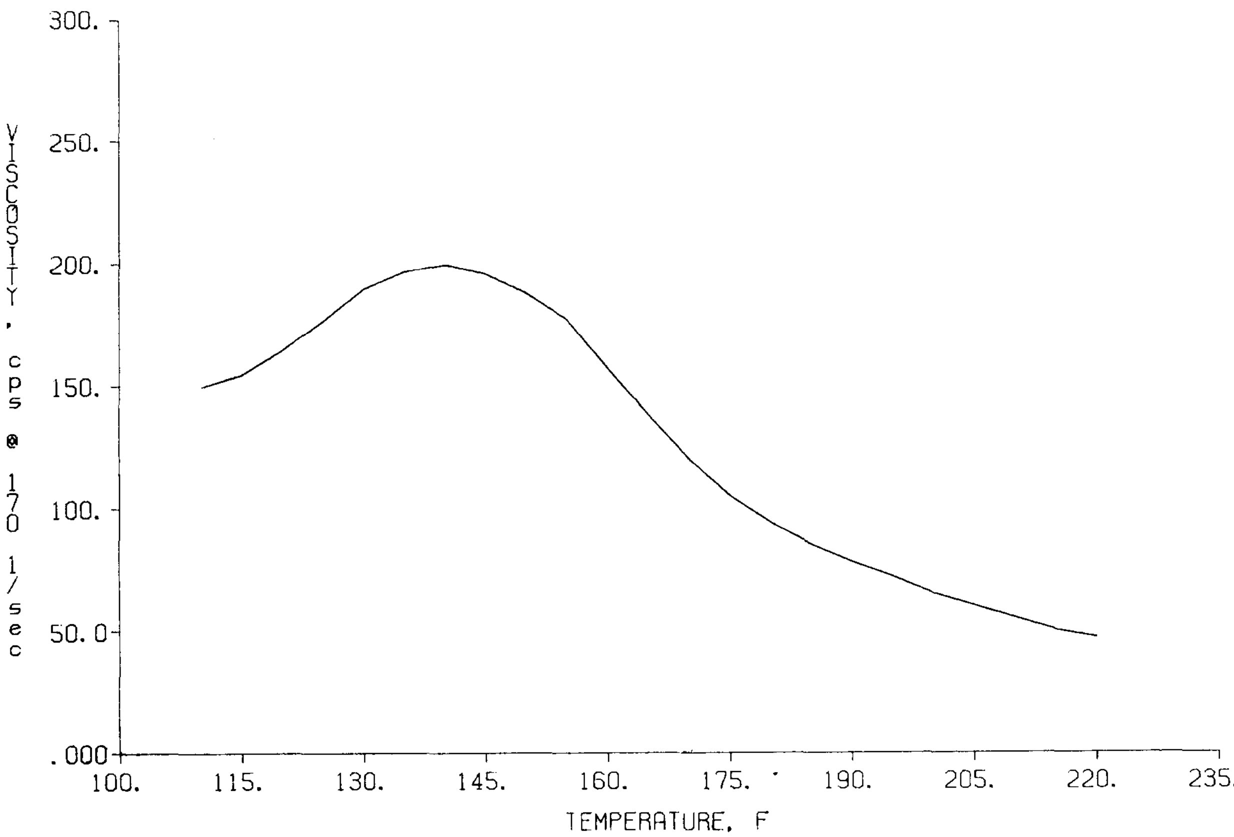

FIGURE 3 — RHEOLOGY OF PROPRIETARY CROSSLINKED ACID

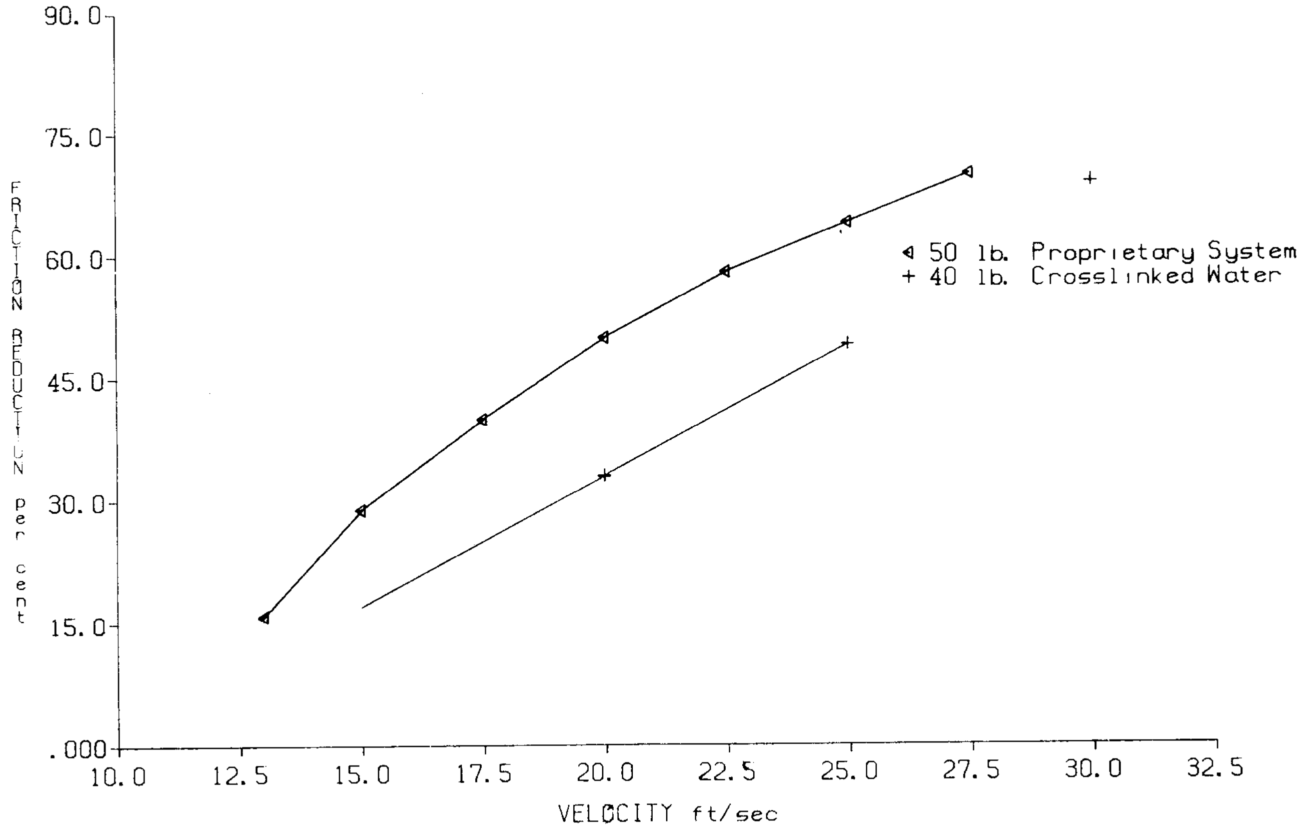

FIGURE 4 -- PROPRIETARY SYSTEM FRICTION REDUCTION

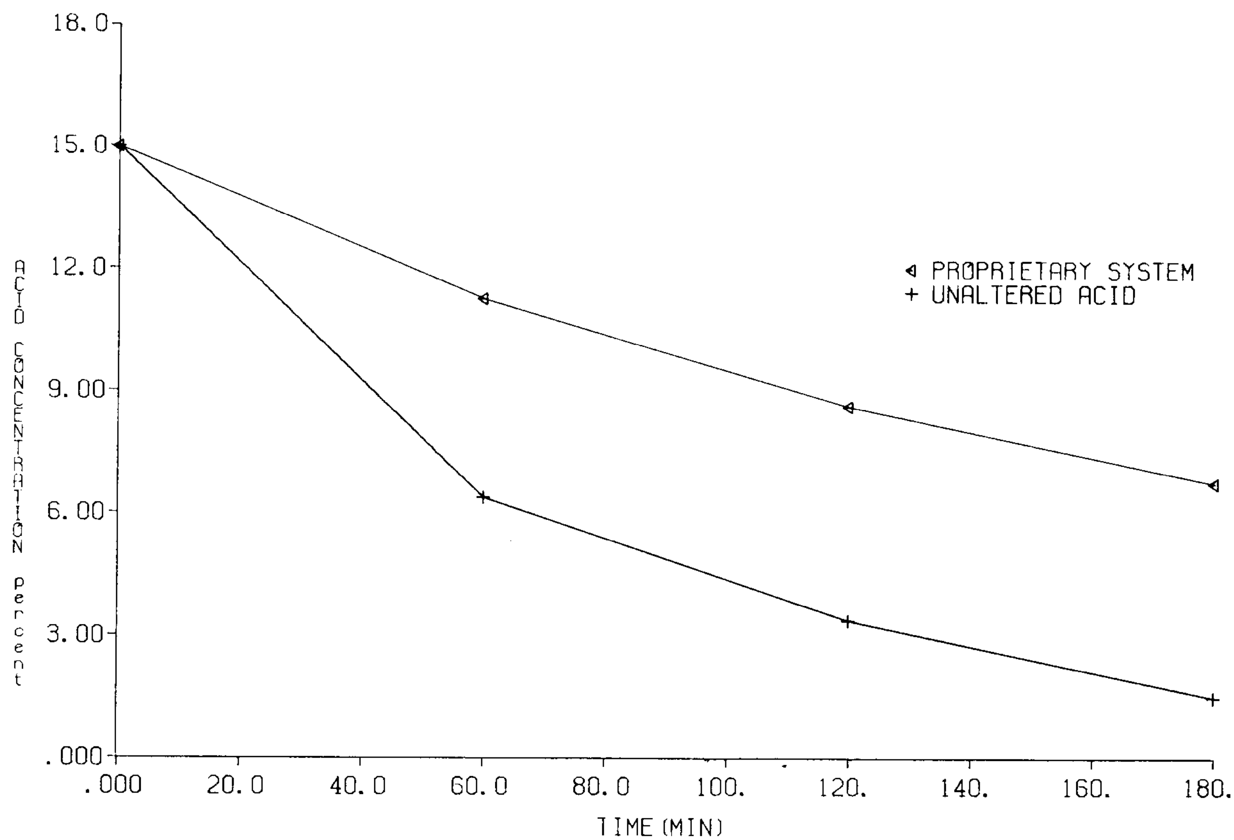

FIGURE 5 -- ACID SPENDING RATE AT 150 F

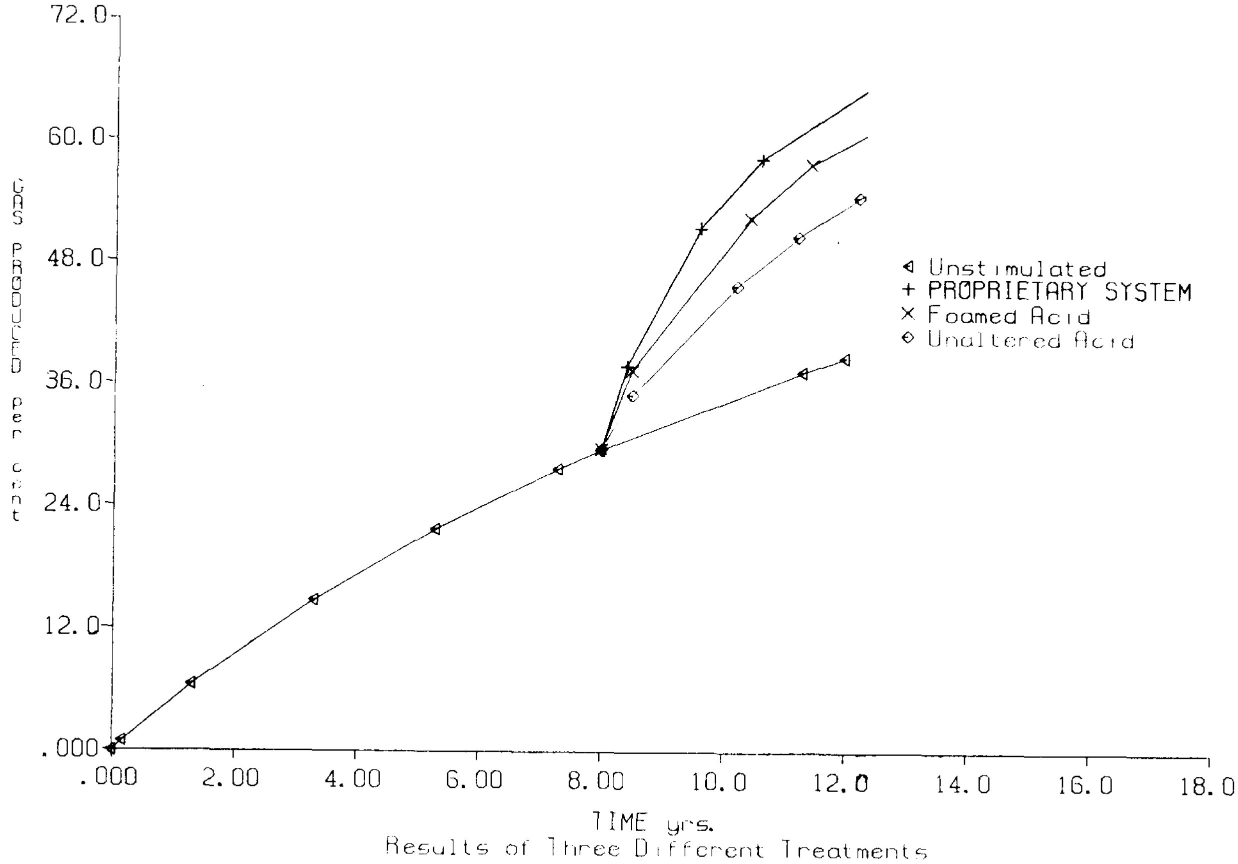

FIGURE 6 -- GAS PRODUCED AS PERCENT OF GAS IN PLACE

TABLE 1
STATIC PROPPANT FALL RESULTS

TYPE OF PROPPANT	TEMPERATURE (°F)	FLUID TYPE	PROPPANT FALL RATE (FT/MIN)
20/40 Sand	75	Crosslinked 15% HCl	*
20/40 Bauxite	75	Crosslinked 15% HCl	.00009
20/40 Sand	140	Crosslinked 15% HCl	.00029
20/40 Bauxite	140	Crosslinked 15% HCl	*
20/40 Sand	175	Crosslinked 15% HCl	*
20/40 Bauxite	175	Crosslinked 15% HCl	.00009
20/40 Sand	75	Crosslinked 28% HCl	.00033
20/40 Bauxite	75	Crosslinked 28% HCl	.00033
20/40 Sand	140	Crosslinked 28% HCl	*
20/40 Bauxite	140	Crosslinked 28% HCl	.00009
20/40 Sand	175	Crosslinked 28% HCl	.00164
20/40 Bauxite	175	Crosslinked 28% HCl	.00492

* No measurable sand fall observed

TABLE 2
STATIC REACTION RATE OF 15% HCl ACID AT 110° F

FORMATION	DEPTH	CONCENTRATION OF HCl AFTER 30 MINUTES REACTION			CONCENTRATION OF HCl AFTER 60 MINUTES REACTION		
		UNALTERED	GELLED	X-LINKED	UNALTERED	GELLED	X-LINKED
A. Noodle Creek	2859' ± 12'	8.3 ± 1.7	8.6 ± 1.7	13.5 ± 0.8	8.1 ± 1.5	8.2 ± 1.6	12.5 ± 0.8
B. Clearfork	6096' ± 434'	7.3 ± 0.4	8.1 ± 0.9	14.4 ± 0.4	6.9 ± 0.5	7.1 ± 0.5	12.9 ± 1.2
C. San Andres	4369' ± 599'	8.0 ± 0.7	7.7 ± 0.5	12.6 ± 0.5	7.8 ± 0.6	7.0 ± 0.7	12.4 ± 0.6

A. Calcite primary @ 92% average

[redacted]

TABLE 3
DYNAMIC REACTION RATE OF 15% HCl ACID WITH CLEARFORK FORMATION AT 110° F

Concentration of HCl Acid

TIME (min.)	UNALTERED	GELLED	X-LINKED (with Breaker)
60	11.5	13.8	14.8
120	11.3	13.3	14.4
180	10.5	12.5	13.7

DYNAMIC REACTION RATE OF 15% HCl WITH PURE LIMESTONE AT 150°F

Concentration of HCl Acid

TIME (min.)	UNALTERED	CROSSLINKED	X-LINKED (with 0.024% Breaker)
60	6.375	11.25	9.75
120	3.375	8.625	6.375
180	1.500	6.75	5.250

DYNAMIC REACTION RATE OF 15% HCl WITH PURE LIMESTONE AT 175°F

Concentration of HCl Acid

TIME (min.)	UNALTERED	X-LINKED (with Breaker)
60	1.125	6.75
120	0.0	3.375
180	0.0	3.00

TABLE 4
COMPUTER SIMULATION RESULTS

		ETCHED LENGTH (FT.)	
FORMATION	INJECTION RATE (BPM)	UNALTERED 15% ACID	X-LINKED 15% ACID
Seven Rivers	15	248	346
Penn Detrital	6	212	536
Cisco	30	191	363
Canyon	30	271	547
Clearfork	20	181*	250*

(BASED ON 100% LIMESTONE UNDER THEORITICAL CONDITIONS)[4]

10	125	404
20	158	837
30	167	1201

* 20% Acid

TABLE 5
RESERVOIR SIMULATOR DATA

A. Formation Properties

Matrix	:	30% Limestone - 70% Dolomite
Porosity	:	7%
Depth	:	8860 ft.
Reservoir PSI	:	2800 psi
Well Spacing	:	320 acres
Poisson's Ratio	:	.28
Permeability	:	.5 md
Formation Height	:	25 ft.
Reservoir Temperature	:	158^{o}F
Frac Gradient	:	.9 psi/ft.

B. Well Description

Tubing OD	:	3.5 in.
Casing OD	:	5.5 in.
Number of Perfs.	:	50
Perforation Diameter	:	.394 in.
Wellhead Flowing PSI	:	700 psi

C. Treatment Variables

Injection Rate	:	20 BPM
Total Acid Volume	:	20,000 Gal.
Acid Strength	:	28% HCl

D. Treatment Fluids Schedule

Case I :
- a. Pump 20,000 gallons 28% HCl
- b. Displace to perfs.

Case II :
- a. Pump 4,200 gallons of 28% HCl
- b. Pump 15,800 gallons of 28% HCl foamed to 70 quality
- c. Displace to perfs.

Case III :
- a. Pump 10,000 gallons 28% proprietary crosslinked acid system
- b. Pump 10,000 gallons 28% HCl
- c. Displace to perfs.

TABLE 6
RESERVOIR SIMULATOR ECONOMICS

ECONOMICS

Case I (Unaltered Acid)	-	$151,500 2 Yr. Yield $1.19 (million)
Case II (Foamed Acid)	-	$277,500 2 Yr. Yield $1.34 (million)
Case III (Proprietary Crosslinked Acid)	-	$166,500 2 Yr. Yield $2.01 (million)

TABLE 7
PROPRIETORY CROSSLINKED ACID RESULTS

WELL #	COUNTY, STATE	FORMATION, DEPTH (FT) BHT OF	JOB DESCRIPTION WELL TYPE	GALS. % HCl AND % OVERFLUSH	AVERAGE RATE PRESSURE	PRODUCTION BEFORE	AFTER 60 DAYS
1	Lea, New Mexico	Seven Rivers, 3282 100°F	Acid Fracturing Injection Well W/O	15,000 Gal. Crosslinked Acid 15% HCl 0% Overflush	15 BPM 1550 PSI	293 BPD 800 PSI	1140 BPD 500 PSI
2	Ward, Texas	Pennsylvanian, 8672 127°F	Acid Fracturing Oil Well W/O	10,000 Gal. Crosslinked Acid 15% HCl 500 Gal. 15% HCl 0% Overflush	6 BPM	70 BOPD	110 BOPD
3	Lea, New Mexico	Wolfcamp, 11,551 180°F	Breakdown Oil Well New	8,000 Gal. Crosslinked Acid 20% HCl 500 Gal. 20% HCl 0% Overflush Fracture Treatment Follow	8.3 BPM 6500 PSI	-0-	200 BOPD Field Avg. 80-90 BOPD After Treatment
4	Sterling Co., Tx.	Lower Canyon, 8082 Upper Canyon, 7822 165°F	Acid Fracturing Oil Well New	68,000 Gal. Crosslinked Acid 3% HCl 180,000 Lbs. 20/40 Sand up to 6 ppg. 0% Overflush	30 BPM 1700 PSI	-0-	230 BOPD 672 MCF/DAY Field Avg. 135 BOPD, 800 MCF
5	Lea, New Mexico	Seven Rivers, 3360 150°F	Acid Fracturing Oil Well W/O	10,000 Gal. Crosslinked Acid 500 Gal. 15% HCl 0% Overflush	11.5 BPM 2800 PSI	11 BOPD 49 BWPD	(6 Months) 20 BOPD 71 BWPD
6	Hale, Texas	Clearfork, 6850 105°F	Acid Fracturing Oil Well W/O	500 Gal. 20% HCl followed by 10,000 gal. Crosslinked Acid 20% HCl 0% Overflush	20 BPM 730 PSI	170 BOPD 380 BWPD	(30 Days) 350 BOPD 1287 BWPD
7	Winkler, Texas	San Andres, 3220 100°F	Acid pad, Acid Fracturing Injection W/O	2150 Gal. 15% HCl 3750 Gal. Crosslinked Acid 15% HCl 2 stages, block with rock salt	4 BPM 2000 PSI	294 BPD 785 PSI 18/64 choke	240 BPD 330 15/64 choke
8	Winkler, Texas	San Andres, 3220 100°F	Acid pad, Acid Fracturing Injection W/O	2150 Gal. 15% HCl 3750 Gal. Crosslinked Acid 15% HCl 2 stages, block with rock salt	4 BPM 2000 PSI	0 BOPD (show)	9 BOPD