A NEW METHOD OF ACIDIZING OR ACID FRACTURING: CROSSLINKED ACID GELS.

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ABSTRACT

Acid Polymer gels having pH less than one have been crosslinked for retarding the chemical and physical activity of hydrochloric acid on calcareous formations. Hydrochloric acid concentrations from ½ percent to 28 percent have been successfully crosslinked. This new and unique stimulation fluid offers high viscosity with adequate shear stability, perfect support for proppants and clay stabilization. Additionally, the fluid provides effective fluid loss control and retardation of acid reaction enabling live acid to penetrate deeper into the formation for better formation conductivity and practically a residue free break for rapid clean-up of the well after the job.

Results of lab and field tests show this new Acid Crosslinked System to be effective stimulation fluid for acidizing and acid fracturing in calcareous and sandstone formations having low formation permeability.

INTRODUCTION

The use of acids to stimulate subterranean formations by acidizing or fracture-acidizing is widely known. A wide variety of techniques and compositions have been practiced, for example: the use of high concentration, i.e. 28 percent hydrochloric acid, the use of weak HCl - HF acids, acid-in-oil emulsions, chemically retarded acids, gelled acids, foamed acids etc.

Different acid gel compositions have been used in acidizing or fracture acidizing of calcareous and sandstone producing formations. However, these acid gel systems do not crosslink the acid polymer; thus, the gel systems are actually sols. As a result, the acid gel system(s) break in a relatively short period of time, dropping proppants. This causes the acid to be quickly spent near the wellbore area thereby limiting the effective penetration of the live acid deeper into the formation and limiting the acidizing treatment to the removal of near wellbore formation blockage.

None of the prior art teaches the formation of crosslinked acid gels having a pH less than one in order to retard the activity of an acid when injected into a reservoir. This retardation of activity allows the acid to penetrate deeper into the formation prior to its activity being spent. The crosslinked acid gel breaks down as a result of time and/or temperature of the reservoir to totally release the activity of the hydrochloric acid and allowing live acid to react with the formation. Additionally, the higher viscosity and shear stability of this crosslinked acid gel are advantageous to fracture-acidizing operations because the crosslinked acid gel produces wider and longer fractures in low permeability carbonate formations. The crosslinked acid gel is also more effective in carrying propping agents into the formation. The system further provides excellent clay stabilization, emulsion prevention and insurance against acid corrosion, in addition to providing fluid loss control and low friction pressure losses.

This new crosslinked acid gel system is effective for calcareous formations with bottom-hole temperatures up to 200°F (93·3°C). The stability of the system decreases with increase in temperature and acid concentrations. To increase the thermal stability of the system in wells with temperature more than 200°F (93.3°C), a preflush to cool the formation is recommended.

The crosslinked acid gel system is basically composed of desired concentration of hydrochloric acid, (¼ percent to 28 percent), a proprietary water soluble polymer, a proprietary water soluble crosslinking agent and an effective acid inhibitor.

EXPERIMENTAL DATA

STABILITY TESTS:

The stability tests were carried out by dividing the acid crosslinked fluid into two portions. One half was kept at room temperature, and the other half was kept in a waterbath at 200°F (93·3°C) with marble chips representing the formation, to spend the acid after breaking the gel. With temperature and time, the crosslinked fluid changes to a high viscosity fluid and finally breaks to a low viscosity fluid. The time of crosslink breaking/stability was noted in each case. Also noticed was whether the spent acid or broken crosslinked fluid develops any kind of precipitate or leaves solid material which may prove to be responsible for impairing formation permeability. The tests were carried out with different concentrations of HCl acid i.e. 3 percent to 28 percent HCl.

TABLE 1—CROSSLINKED STABILITY

HCl Acid conc. (%)	Room Temp; 68°F (20°C)	200°F (93.3°C)	Remarks
3	>48 hrs.	>4 hrs.	Practically no solids on breaking.
5	>38 hrs.	>3 hrs.	
7½	>23 hrs.	2 hrs.	
10	>12 hrs.	2 hrs.	
15	> 8 hrs.	1½ hrs.	
20	>2½ hrs.	3/4 hr.	
28	30-40 mins.	15-20 mins.	

The stability at elevated temperature will further increase due to cooling of the formation by the crosslinked fluid being pumped. This stability time of the different strengths of acid crosslinked fluid is sufficient enough to place the crosslinked fluid into the formation and get a break in the shortest possible time with rapid well clean-up after the job. However, it may be mentioned that if a further increase in stability time is required a preflush to cool the formation and/or incorporation of a suitable gel stabilizer is recommended.

Clay Swelling Tests:

For the purpose of clay swelling tests, the following procedure was followed:

The crosslinked acid @15 percent was treated with white marble chips to spend the acid on breaking; 25 ml of this spent acid was filtered and placed in a tall slender 11 dram vial. To this acid solution 0.2 grams of dry bentonite clay was added. The tendency of the clay to fall and disperse in the solution was noted along with the settling height of the clay after 24 hours. The tests were also carried out with live acid after breaking the crosslinked fluid. The test was repeated with tap water and a 2 percent KCl solution for the sake of comparison. The observations are tabulated below.

TABLE 2—OBSERVATIONS

Sequence No.	Test Fluid	Status of Soln./Acid	Dropping Tendency	Dispersing Tendency	Settling Height in mm
1	Tap water	Fresh	Poor	Poor	4.0
2	2% KCl in tap water	Fresh	Good	Good	2.5
3	15% cross-linked HCl acid with additives*	Spent Acid	Good	Good	1.5
4	" "	Live Acid	Good	Good	1.5

*Additives include acid corrosions inhibitor and non-emulsifier.

These results indicate that the system also provides effective anti-clay swelling properties.

Sand Suspension Tests:

The sand suspension tests were conducted to evaluate the effective support for sand (propping agent) by the acid crosslinked system at different temperature ranges 80°F to 200°F. (26.67°C to 93.3°C). For this purpose, the tests were carried out with the crosslinked fluid of different HCl acid concentrations. The acid at a desired concentration was cross-linked and to this 20-40 mesh Ottawa sand was added in a Waring blender and mixed thoroughly. The fluid with the sand mixture was transferred to a graduated cylinder and kept in a water bath at the test temperatures. The observations were made for the time of sand separation and settling at the bottom of the measuring cylinder. These observations are recorded in Table 3.

TABLE 3

Conc. of Acid Cross-linked System	20-40 Mesh Sand Conc.	80°F (26.67°C)	100°F (37.78°C)	150°F (65.56°C)	200°F (93.3°C)
3% HCl	4 lbs./gal	>28 hrs.	20 hrs.	3-4 hrs.	2-3 hrs.
5% HCl	" "	>28 hrs.	6 hrs.	1½-2 hrs.	1¼-2 hrs.
7½ HCl	" "	>20 hrs.	6 hrs.	1¼-1½ hrs.	1-1½ hrs.
10% HCl	" "	>10 hrs.	2½ hrs.	1-1½ hrs.	1-1¼ hrs.
15% HCl	" "	> 6 hrs.	1½ hrs.	1 hr.	45-60 mins.
20% HCl	" "	1½ hrs.	1 hr.	40-60 mins.	30-60 mins.

These tests indicate that the acid crosslinked system at different acid concentrations provides perfect support for the sand column. However, the time of sand separation is accelerated with the increase in temperature and concentration of HCl acid. The cooling of the fracture faces due to preflush and crosslinked fluid will further lengthen the sand separation time.

The sand was added to the crosslinked fluid in a Waring blender and mixed at high speed for about 30 minutes and transferred to a graduated cylinder. The sand remained suspended in the crosslinked fluid indicating shear stability of the crosslinked fluid.

Reaction Rate Study:

The Reaction Rate tests were carried out to evaluate the retardation effect the crosslinked acid has on the limestone formation. In absence of a reaction rate autoclave, the tests were performed with the acid formulation using white marble chips in an open beaker. The test conditions were as follows:

Pressure--------------------------------Atmospheric
Temperature-----------------------------100°F (37.78°C) and 200°F(93.3°C)
Marble chips 8-10 mesh------------------80 gms.
15% HCl acid with additives-------------200 cc.

Stirring was done to insure complete and dynamic contact. The acid volume to rock surface area simulated a fractured width of 0.24 inches. The reaction rate tests were also made with 15% inhibited HCl acid for comparison.

The crosslinked acid was placed in a beaker and marble chips were added. While constantly stirring, the beaker was kept in a water bath at the test temperature. At regular time intervals of 3, 6, 12, 24, 48, minutes the sample was drawn and titrated against a standard 1N NaOH solution.

TABLE 4

Temperature = 100°F(37.78°C) Acid Strength-Percent			Temperature = 200°F (93.3°C) Acid Strength-Percent		
Elapsed Time in Minutes	15% Inhibited HCl Acid	15% Cross-linked HCl Acid	Elapsed Time in Minutes	15% Inhibited HCl Acid	15% Cross-linked HCl Acid
0	15.0	15.0	0	15.0	15.0
3	10.0	13.0	3	5.5	10.0
6	7.0	11.3	6	2.0	8.0
12	2.8	9.1	12	0.3	5.2
24	0.5	6.2	24	--	2.4
48	--	3.1	48	--	0.6

Retardation is achieved on white marble chips with the acid crosslinked system. The above tabulated data has been plotted in graph numbers 1 and 2.

Reology Data:

The reological properties of the acid-gel crosslinked system has been determined using a Fann Viscometer Model 35A, as per API,RP-39 method. A graph of acid crosslinked viscosity and gel viscosity versus temperature has been plotted in figure 3. The test data are as follows in table 5.

TABLE 5—DIAL READINGS AT INDICATED TEMPERATURE

Strength of Acid-Gel Cross-linked System	80°F (26.67°C)		100°F (37.78°C)		125°F (51.67°C)		150°F (65.56°C)	
	600rpm	300rpm	600rpm	300rpm	600rpm	300rpm	600rpm	300rpm
5%	>300	290	>300	270	>300	210	210	107
10%	245	200	215	180	185	115	130	75
15%	230	195	195	160	85	105	50	33
20%	150	88	80	68	55	28	28	20

The rheological data obtained with Fann Viscometer, Model 35A will be verified with Fann-50C for more specific evaluation of the system.

FIELD RESULTS

At the time of writing this paper, field results could not be received as expected and therefore field results will be included at the time of the paper presentation.

CONCLUSION

Suitability of the new acid crosslinked system for the wells completed in limestone and dolomite reservoirs with low formation permeability having a bottom-hole temperature of 200°F (93.3°C) have been established by the laboratory tests. All the tests have been carried out with different concentrations of HCl acid; e.g. 3 percent HCl to 28 percent HCl. The system provides excellent potential for crosslinking weak acids (3 percent to 7.5 percent) to effectively treat and/or breakdown calcareous as well as sandstone formations.

This new system provides an effective treating fluid which offers the following:

- (i) High viscosity and adequate shear stability to enable it to be used for fracturing.
- (ii) Perfect support for (sand column) proppants.
- (iii) Expected low friction pressure.
- (iv) Retardation of acid reaction, enabling live acid to penetrate deeper into the formation for achieving better formation acidized conductivity.
- (v) Expected fluid loss control.
- (vi) Clay stabilization.
- (vii) Non-emulsifying properties.
- (viii) Acid corrosion inhibition.
- (iv) Clean and residue-free gel break to less than 10cp viscosity for rapid clean-up of the well after the job.

The additives/surfactants used in the formulation are compatible with different strengths of HCl acid. The reaction rate data indicates that the system provides effective retardation of acid reaction on limestone and dolomite formations, thus permitting the live acid to penetrate deeper into the formation to obtain better formation conductivity. The sand suspension tests show that the system is characterized by perfect suspension of proppant column which provides good proppant carrying ability. The corrosion tests and emulsification tests indicates that the system has effective corrosion inhibition and nonemulsifying properties. The clay swelling tests show that the formulation also provides anti-clay swelling properties.

The stability of the acid crosslinked system depends on the strength of HCl acid and the temperature. Higher the strength of HCl acid and temperature the lower the stability. The amount of crosslinking agent varies with the strength of HCl acid i.e. higher the strength of acid, the more the crosslinking agent required. The stability at higher temperatures can be increased by cooling the formation with suitable pad fluid and also by incorporating suitable gel stabilizer.

SUMMARY

The crosslinked acid gel system can be utilized for acidizing or fracture-acidizing to stimulate oil and gas wells completed in calcareous or sandstone formations with low formation permeability. This system should be considered for any treatment that requires large fracture widths, deep penetration of live acid, high proppant concentration, (2-8 pounds/gallon) clay stabilization, emulsion prevention and clean solids free broken fluid. The system works in different concentrations of HCl acid such as ¼ percent to 28 percent HCl acid. The amount of crosslinking agent varies with the acid concentration. At room temperature, the stability of the acid crosslinked gel depends on the acid concentration. For HCl acid concentration 3 percent to 10 percent, the fluid is stable for about 12 to 48 hours, and for 15 percent to 28 percent, the fluid is stable for about 1 to 8 hours at room temperature, 68°F (20°C). At 200°F (93.3°C) the fluid with 3 percent to 10 percent HCl concentration breaks in about 2-4 hours and the crosslinked 15 percent to 28 percent HCl acid breaks in about ½ to 1½ hours to less than 10 cps viscosity with practically clean solid-free fluid.

The laboratory tests proved that the system provides good clay stabilization, perfect support for sand column compatibility with most acid additives, delayed reaction rate, inhibition of formation damage and has adequate shear stability to enable it to be used for fracturing.

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ACID STRENGTH VS. TIME
GEORGIA WHITE MARBLE
(Acid Crosslinked System)

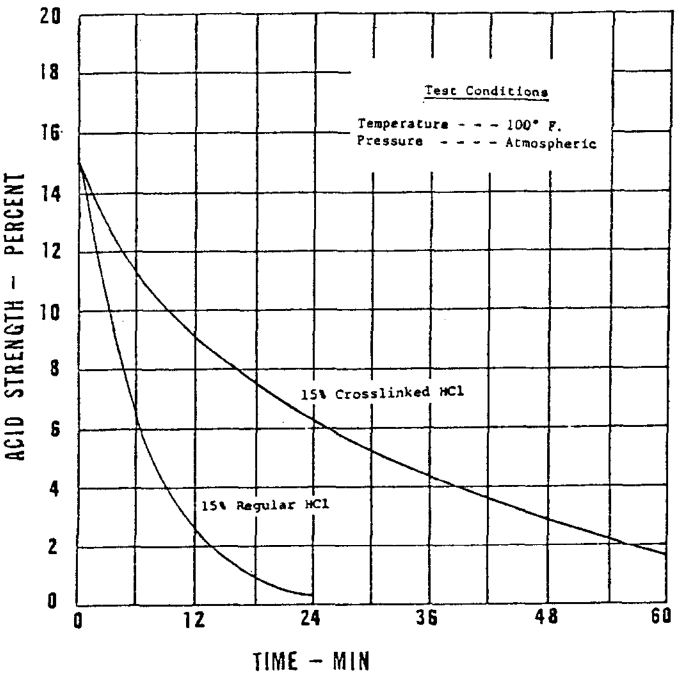

FIGURE 1

ACID STRENGTH VS. TIME
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(Acid Crosslinked System)

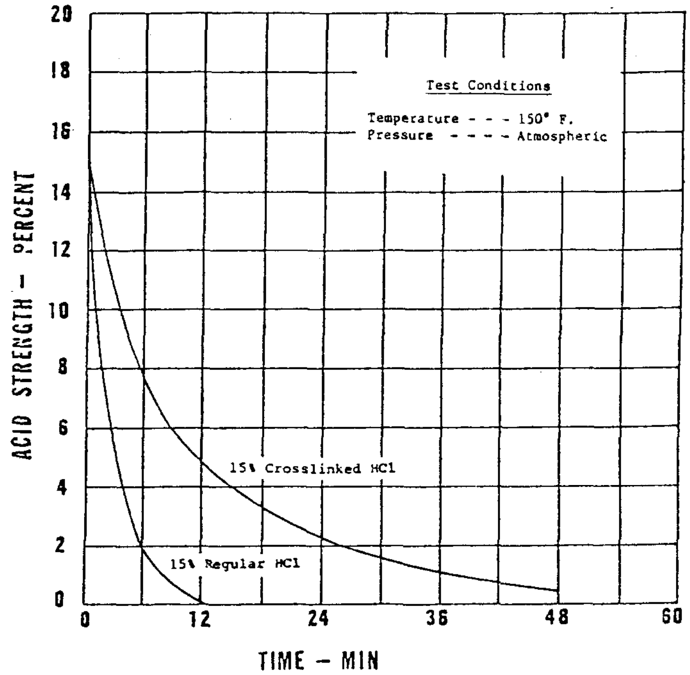

FIGURE 2

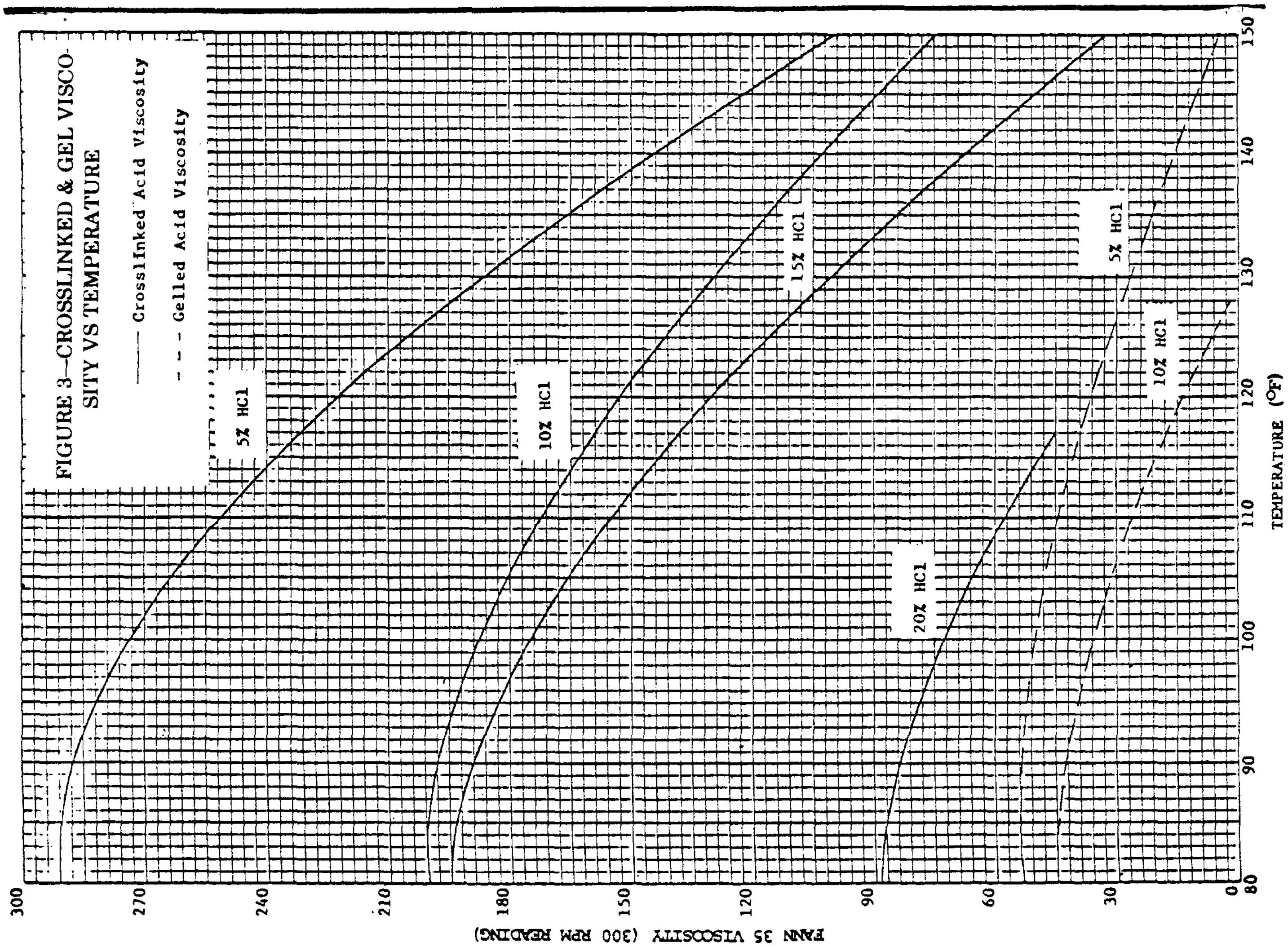

FIGURE 3—CROSSLINKED & GEL VISCOSITY VS TEMPERATURE